the glass industry

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# The Glass Division—
## at the 58th Annual ACS Meeting

The American Ceramic Society's Annual Meetings continue to grow and expand. Over twenty-five hundred ceramists, friends, and wives gathered at the Statler Hotel in New York, during the week of April 21-25, to participate in the varied program presented by the many divisions of the Society.

The glass division provided thirty-one papers related directly to glass and refractories. The visitors from overseas gave an international flavor to the meeting. Among the visitors were: Dr. Pierre Ivan Peyche, director of research, and P. La Burthe, chief engineer, both of Saint-Gobin, Paris; Hideo Yamamoto, Asahi Glass Company, and L. A. Thomas, G. E. Research Laboratories, Wembley, England.

The extremely interesting program of papers included technical, theoretical, and practical aspects of the industry. The committee follows:

John W. Michener, Chairman, Owens-Corning Fiberglas Corp., Newark, Ohio.

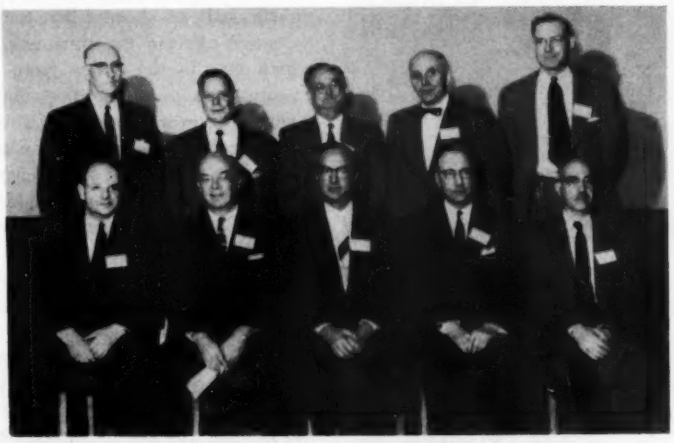
Frank R. Bacon, Owens-Illinois Glass Co., Toledo, Ohio.

Orson L. Anderson, Bell Telephone Labs., Murray Hill, N. J.

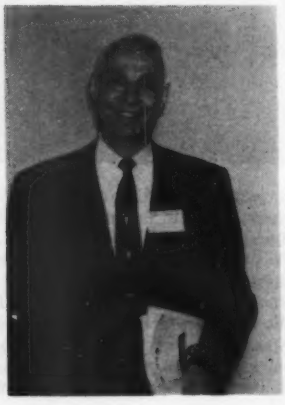
The Monday afternoon session was introduced by J. W. Michener, Owens-Corning Fiberglas Corporation, who was very successful in keeping the program on schedule by using a time clock. This innovation is recommended for future meetings.

The first paper, "Morphology of Fractures in Polished Glass Surfaces," by W. C. Levengood and W. E. Fowler, Libbey-Owens-Ford Glass Company, Toledo, Ohio, was presented by W. C. Levengood.

The previous work of Bielby, French, Preston, and others was reviewed and the so-called "bridging over" phenomena was discussed. The authors described a breath-figure technique that was applied to the study of the effect of polishing on fracture patterns in glass surfaces. Unusually good photographs were shown (at 100X magnifications) of cracks on glass before and after polishing. The experiments showed that the apparent controversy concerning the polishing out or "bridging over" of surface fractures may be explained on the basis of crack dimensions. If the fracture width is less than $\frac{1}{4}\lambda$, it may be sealed over by polishing, even though the depth may be a millimeter or more. The



**Officers of the American Ceramic Society, installed at the 58th Annual Meeting. (Seated left to right): Treasurer, Andrew Pereny, Pereny Equipment Co.; Vice president, Oscar G. Burch, Owens-Illinois; President, Karl Schwartzwalder, A C Spark Plug Div., General Motors; Vice president, Christian W. Planje, Gladding, McBean & Co.; Vice president, Louis Navias, Gen. Electric Laboratories. (Standing): Trustee, Charles M. Dodd, Iowa State College; Trustee, Lane Mitchell, Georgia Inst. of Technology; President-Elect, John F. McMahon, State University of N. Y., College of Ceramics at Alfred University; Trustee, Leonard G. Chering, Preston Laboratories; and Trustee, Harry W. Thiemecke, Homer Laughlin China Co.**



information indicated that the scratch was partially healed over by a thin layer of glass. A modified condensation chamber was devised in which moisture was permitted to condense on the surface forming a breath-like figure that tends to exaggerate the aging effect and thus permitting a more detailed study of the fracture growth in a polished surface. Curves in which the fracture growth was plotted, against time, showed the relationship to be linear.

The second paper of the afternoon was: "Semi-chemadsorbed Oxygen Monolayers and Non-Wetting Glass Surfaces," by Scott Anderson, Anderson Physical Laboratory, Champaign, Illinois.

This paper was devoted to the very important phenomena of wetting of glass surfaces. Silicate glasses were prepared which can support a drop of water with a contact angle of the order of 90°. Several of these were investigated and found to owe this property to a monolayer of oxygen, bound to the surface with a bond of the order of 40 kcal/mol. Certain dyes, when adsorbed on the glass surface, were found to be specific to oxygen gas. Complicated apparatus was used and the glass sample was first heated and then outgassed. The oxygen concentration was determined by its quenching of the phosphorescence of trypaflavine dye. The results showed pronounced differences in the wetability of soda-lime-glass, lead, glass, and soda-lime glass coated with $TiO_2$.

The next paper, "The Amorphous Surface Layer on Finely Ground Crystalline Quartz", by J. G. Sayre and J. W. Michener, Owens-Corning Fiberglas Corporation, Newark, Ohio, was presented by Dr. Sayre.

A technique was devised in which electron microscopy was applied to a study of the amorphous layer of finely ground crystalline quartz. The thickness of the amorphous (Beilby) surface layer was investigated with the selected area diffraction stage of the electron microscope. This technique offers a means of direct particle size determination and subsequent electron diffraction from an individual particle. Diffraction patterns of the fine quartz particles showed that the method of reducing particle size affected the thickness of the amorphous layer, which was in the range from 500 to 1000 angstroms. Examination of other crystalline particles indicated the layer to be even thinner for some materials. There was no apparent boundary between crystalline and amorphous area. The excellency of the electron micrograph pictures indicated that this constantly improving technique provides an extremely useful tool with which to enhance the study of glass surfaces.

The next paper, "Stress Measurement in Cylindrical Vessels", was by H. N. Ritland, Corning Glass Works, Corning, New York.

Stress measurements and stress analysis in glass have become increasingly important to the user and manufacturer. An improved technique was described in which the sample was not mutilated or destroyed and in which

the actual stress of the various cylindrical objects could be observed. An analysis was presented of the birefringence patterns observed in the walls of cylindrical glass objects when viewed tangentially in a matching index fluid. The patterns to be expected from combination of parabolic and bending stresses, resulting from asymmetric cooling, were calculated and experimentally measured patterns shown to illustrate the theory. A simple method was presented whereby the stresses at the outside and inside surfaces of tempered ware may be calculated from the observed pattern. Fundamental data were given to indicate ideal, poor, or good heat treatment. It was suggested that the method might also be applied to routine testing or control test.

The phenomena of viscous flow, especially as applied to glass-to-metal seals, was the subject of the next paper, "Viscous Flow in Glass-to-Metal Seals", by H. E. Hagy and H. N. Ritland, Corning Glass Works, Corning, New York. Mr. Hagy made birefringence measurements on glass-to-metal seals with simple geometries of the sandwich-seal and bead-seal types. The measurements were made during cooling and various constant rates. Thermal contraction data were obtained on the metal and on the glass while cooling at the same rates. Through the use of these data, the viscosity of the glass was calculated as a function of temperature and cooling rate. Viscous flow in the seal was observable at temperatures as much as 100° C. below the strain point. It was shown that the thermal stress of glass is rate-dependent in cooling while the metal is not. The observed setting points were given as 434-451° C. for different rates of cooling. Absolute viscosity data were also compared with different rates of cooling. Glass compositions which were simple glass were given. These data are fundamental and important to the problems occurring in complicated glass-to-metal seals.

The next paper was a highly theoretical one given by H. T. Smyth—"Theory of Viscous Flow of Glasses", Rutgers University, School of Ceramics, New Brunswick, New Jersey. A quantitative theory of viscous flow was worked out based on mathematical treatment. Stresses in glass first produced an extension in fibers parallel to stress and a comparison at right angles to the applied stress. A calculation of strain in each direction provided means of knowing which bonds were broken. The essential mechanism was assumed to be a specific change of neighbors around either an unsaturated silicon or a nonbridging oxygen. The elastic displacement around such a change was computed and can be shown to give rise to flow. The important fact appeared to be that certain bonds break. On the basis of elastic theory a solution of these breaks was illustrated schematically. The theory indicated how viscosity may change with time at constant temperature and also explained the viscoelastic effects which show up when a sample is first loaded. The relation between the viscoelastic effects and certain structural parameters can thus be deduced.

The next paper, "Effect of Stress During Forming on the Strength of Glass", by E. D. Lynch and F. V. Tooley, Department of Ceramic Engineering, University of Illinois, Urbana, Illinois, was devoted to a study of certain factors involved in the preparation of samples for strength measurements. The paper was presented by Mr. Lynch. The effect of mechanical stress applied during the drawing process on the level of strength obtained was determined for large diameter fibers (43-50 mils dia.) of soda-lime-silica glass. The results indicated that the mechanical stress applied during forming increased the strength of the drawn fibers. Strength measurements were also made on fibers whose surfaces had been abraded by $Al_2O_3$ abrasives. The abraded fibers showed a strength decrease of as much as 18 per cent as compared to the untreated fibers. The tendency toward increased strength resulting from applied force in forming still persisted with the abraded samples. There was no alteration in the density of the glass caused by variations in the forming stress. It was suggested that the variations in strength may be related to the stresses set up in drawing that are not reviewed in the annealing process.

"An Accurate Method for the Study of Ionic Diffusion in Glass", by Rajeshwar K. Gupta and Robert L. Hess, University of Michigan, Ann Arbor, Michigan, was presented by Mr. Gupta. It is believed that the alkali ions are preferentially located in glass, especially at the surface and the following method of testing was proposed: The method used freshly drawn cane of glass as the sample, a dilute solution of hydrochloric acid in double distilled water as the leaching reagent, and a Beckman Model B (Model DU may also be used) Flame Spectrophotometer for measuring the alkali concentrations in the leach solutions. Duplicable results can be obtained even with fairly chemically durable alkali glasses. Results were obtained as the extraction or diffusion rate of each ion separately in well-defined units [gm. of ion/($\sqrt{\text{min.}}$) (sq. in. area)]. The uncertainty in determining the surface area of the reacting sample was eliminated. Thus, it is possible to use the results for activation energy calculations. Diffusion rate results for several glasses, obtained by this method, were reported.

In the study of experimental glasses, a careful procedure involving melting in platinum was used after which the samples were drawn in the form of cane and specimens cut from the cane. It was claimed that samples thus prepared were to be preferred over ordinary powered sample, especially if ion diffusion rates are to be determined.

The Tuesday morning session was devoted to a Symposium on the subject of "Basic Refractories in the Glass Industry", R. J. McEvoy, Owens-Corning Fiberglas Corporation, Toledo, Ohio, was session chairman and the Symposium was a joint session of the Glass and Refractories Divisions. The first paper, "Keynote: Basic Refractories in Glass Tank Furnace Regenerators", by T. B. Montgomery and J. S. Gregorius, Pittsburgh Plate Glass Company, Pittsburgh, Pennsylvania, was given by Mr. Montgomery. Mr. Montgomery pointed out that one of the desirable goals in the glass industry is to prolong the useful life of tank melting furnaces at high tonnage rates, thus effecting substantial economies. The improved preparation of raw batch materials, their controlled mixing, and furnace instrumentation have aided in raising these levels. However, most of the high level of production has been achieved by higher rates of fuel consump-

tion which in turn pose refractory problems.

High levels of production require high rates of fuel consumption which develop high hearth temperatures and high flame velocities. The high temperatures generate flux vapors and the high velocities increase the quantity of batch entrainment. These corrosive substances are carried into the ports and checker packing of the outgoing regenerators at punishing temperatures.

Under such an environment the fire clay refractories of high and superduty character react with the corrosive substances forming slags. These slags drain down to lower checker levels where they ultimately reach freezing temperatures and create massive stoppages. These stoppages are vitally serious even though usually confined to the first two ports.

These circumstances pose the challenge: what refractory substance may be found which will meet these rugged requirements? A possible solution has been demonstrated by the use of basic brick, of which there are a number of different types. Some are a periclase type, some a forsterite type, some a chrome-spinel type, some are chemically bonded, and some are fire bonded. All have intrinsic fusion temperatures of 3400° plus. They do not easily slag with the corrosive vapors and carry-over mentioned above.

There is another consideration which emphasizes the need of a refractory for regenerator and checker packing structure that excels the performance of high and superduty clay-type refractories. It is necessary to bring the melting furnace and its accessories into a more balanced life expectancy. Electro-cast refractories are extending the life span of melting basin and superstructure, and, therefore, the furnace accessories, such as ports, regenerator chambers, and regenerator packing must be brought up to comparable life expectancies. Owing to the extreme low solubility of basic refractory grains in molten glass they are not employed in proximity to the glass bath.

The next paper, "Correlating Glass Furnace Operation and Basic Refractories", was by J. J. Webber, Harbison-Walker Refractories Company, Pittsburgh, Pennsylvania. The operating conditions prevailing in a glass furnace regenerator were reviewed and, the desirability of basic refractories was pointed out. It was also noted that the type of operation will also influence the basic refractory from which one may expect the most economical operation. Operating conditions are classified into two main categories: (1) those related to firing and (2) those related to other operating conditions, such as type of glass being melted and amount of batch material carried over into the regenerators. Stabilization against cyclic oxidizing and reducing atmospheres are of primary importance in the first category, whereas some chemical and physical properties are of greater importance in the second category. Magnesium silicate refractories with a high degree of stability are particularly applicable in the first category. Magnesium silicate or chrome-magnesite compositions may be applicable in the second category.

Practical tests were developed to stimulate commercial use. A cyclic test in which alternate oxidizing and reducing conditions were maintained proved most valuable. The results of exposure to as much as 700 cycles showed the superiority of stabilized forsterite. The results were consistent with service tests made in generator chambers. Petrographic studies have been of considerable aid in evaluating various refractories.

Photos by Hugh L. Kline

The next paper of the Symposium, "Mineral Placement of Constituents in Five Types of Basic Brick", was written and presented by N. B. Dodge, United States Steel Corporation, Monroeville, Pennsylvania. This paper was a highly informative one in which a major user of refractories, a steel company, considered the importance of refractories in steel operations. A petrographic examination was conducted on chrome ore, chrome ore-periclase, periclase-chrome ore, periclase, and forsterite brick. Photomicrographs show the size and placement of the various constituents. The petrographic study revealed desirable as well as undesirable structure of certain refractories as related to their use. The effects of firing time and temperature and the structures that were more sensitive to heat shock were illustrated by slides. Other advantages recognized by these studies were evidence of the important part played by the bond in such refractories.

The next paper, "Regeneration Efficiency and Basic Brick in a Glass Furnace", by L. R. Robertson, John J. McMackin, and Frank V. Halvonik, Brockway Glass Company, Brockway, Pennsylvania, was presented by Mr. Robertson. This paper was a most practical one and presented very useful data assembled at commercial plants. The performance of various types of brick in regenerators for glass tanks was discussed. A practical test of evaluation was described which made use of a velocity thermocouple in which the preheating characteristics of certain brick could be ascertained in the checkers themselves. The air preheat cycle as well as waste gas cycle was studied for specific settings. It was shown that as production or furnace pull was increased, the importance of preheating became more apparent. High speed recorders were of considerable value in analyzing the data. Maximum heat storage was found to be best from simple settings, providing a long-path heat flow. Other factors that were found to be desirable were (1) settings with adequate support, (2) ample flue area, (3) walls and arches that are inactive or not dripping. Basic materials have given excellent life and have shown encouraging results. This paper was a most practical one, and such performance data are practical and useful to all plant operators.

"How Long Will Basic Last?", by Mr. Henry E. Walker, Harding Glass Company, Fort Smith, Arkansas, was the next paper. The practical theme of presentation was continued by Mr. Walker who described experiences with various glasses in tanks producing window glass. The paper was greatly enhanced by illustrations comparing the life and type of failure of old fireclay checkers and the newer basic brick checkers. The basic brick, especially the chemically bonded type, showed encouraging results, but it seemed to be highly important to provide a burned basic brick underneath, or as a support, for the chemically bonded brick. It was also pointed out that when basic brick did fail, they appeared to fail in a dry manner in which the dry or dusty material fell through the checker without serious clogging. The importance of design and support was emphasized, and where life expectancy of a year or greater was desired, the basic brick was highly recommended. The paper was augmented by a considerable number of questions that were pertinent to the problem of the use of basic brick.

The next paper, "Basic Brick Applications in High Temperature Furnaces", by C. E. Grigsby and R. G. Abbey, General Refractories Company, Philadelphia, Pennsylvania, was presented in two parts—the first part by Mr. Abbey and the second by Mr. Grigsby. Mr. Abbey took full advantage of pictures and illustrations of various settings to show the definite superiority of basic brick in checker brick settings. The principal difficulties and causes of failure were batch carry-over and spalling. Again its highly recommended that all settings be properly supported by basic brick, and it was indicated that the basket-weave type of setting was the most preferred. It was pointed out that the basic brick have made high rates of production possible and have been necessary for the maintenance of a high rate of pull on the tank.

Mr. Grigsby presented an excellent survey accompanied by numerous illustrations of the latest installations in the steel industry. Although the survey was not confined to the glass field, the close similarity of the applications made it most useful. A number of future designs were illustrated, and some indication of future applications were presented.

The final paper in the Symposium was, "Basic Refractories in Glass Furnace Regenerators," by F. G. Heck, and E. G. Samuels, E. J. Lavino and Company, Philadelphia, Pennsylvania. The paper was presented by Mr. Heck. This paper reported the progress made in the various field tests in which basic brick have been used in the checkers, ports and regenerator walls of borosilicate glass wool furnaces and amber container glass furnaces. Some of the conclusions concerning the amber tank were (1) fully supported base is desirable, (2) basic brick should be extended to offset any attack by carry-over from batch, (3) basket-weave or loose setting is desirable (4) super-structure of basic brick is desirable to avoid drip, (5) mechanical means of wall stabilization are desirable, (6) header construction is desirable (7) wall life of three years or better can be expected if proper construction has been followed, and (8) it is possible that one type of basic brick may be desirable for one type of glass and another type desirable for still another type.

The Symposium was followed by a general discussion and question period in which all the authors participated. The program was well attended and quite popular. Mr. McEvoy is to be congratulated upon the excellent manner in which he handled the entire program.

Wednesday afternoon the Glass Division Program was continued with a paper, "Re-evaluation of the Chemical Durability of Soda-Potash-Silica Glasses", by Rajeshwar K. Gupta and Robert L. Hess, University of Michigan, Ann Arbor, Michigan. Mr. Gupta continued his series of papers on durability and applied the techniques described in the paper, "An Accurate Method for the Study of Ionic Diffusion in Glass," also written by himself and Mr. Hess, to some simple glasses. It was found that the alkali extraction curve for an 18 per cent alkali and 82 per cent silica exhibited a maximum and not a minimum as previously believed. The glasses contained combinations fo soda and potash. The data also revealed that a pure soda-silica glass appeared to hold the sodium ion in the structure more tenaciously than the potassium ions in a pure potash-silica glass. Both glasses contained equal weight per cent of alkali. The effects of the replacement of silica by calcium oxide were also investi-

(*Continued on page* 338)

# Vacuum Fabricated Glass Tubing

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**Abstract**

The forming of precision bore tubing, unusual shapes and complex internal configurations with a high degree of accuracy may be attained by vacuum forming. The process ideally lends itself to laboratory or production work without costly precision equipment. The information set forth provides the necessary techniques for constructing glass devices for specific applications.

**History**

Early work in vacuum forming glass tubing was not intended to produce precision internal dimensions. In 1903, Ernst[1] evacuated a glass tube and then heated the glass, causing it to shrink over an axially centered wire. This effort was intended to obtain a vacuum tight seal for use as lead-in wires on electronic tubes. Haagn[2], in 1906, protected the platinum wire of a high temperature resistance thermometer from polluted atmospheres by imbedding the platinum in quartz. He accomplished this by winding a platinum wire helix over a fused quartz rod and placed this assembly in a long narrow quartz test tube. The tube was evacuated and external heat applied until the outer quartz tube collapsed over the platinum wire and inner quartz rod. Karl Kueppers[3] of Germany contributed greatly to vacuum formed glass tubing. In 1913 he described a method of vacuum forming glass over tapered or shaped metal mandrels. Kueppers accurately applied internal calibrations on glass measuring apparatus by placing graduations on one section of a split tapered mandrel and collapsing the evacuated glass tube by the use of external electric heat. Although the mandrel was undercut, the split construction allowed the mandrel to be removed easily from the shrunk glass. Several years later, Kueppers suggested a method of reinforcing glass tubes. A metal mandrel was wrapped with wire gauze, mesh, or net; the wound mandrel was inserted into a glass tube, evacuated and by external heating, the glass was sealed to the wire mesh.

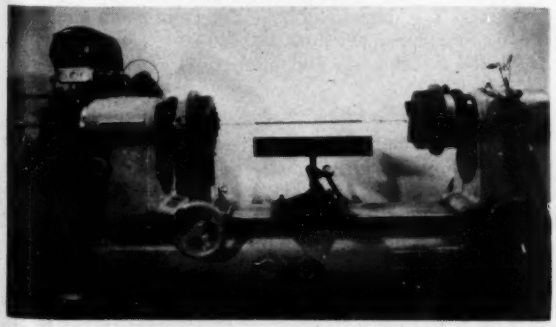

**Fig. 1. Glass tubing may be conveniently vacuum formed on a glass lathe. The setup shown, lends itself to small quantity work and the shrinking is constantly under the operator's control.**

The techniques employed for the construction of precision vacuum formed tubing were not exploited and the inherent advantages never fully realized until about 1935. Accuracy in glass gauges, such as monometers, barometers, and graduated burettes had to be maintained if successful results in research and production were to be duplicated. Vacuum formed precision bore tubing could be held within .0002 inch of required dimension and was the solution employed.

Cox[4], Brewer[5], and Fischer[6] made improvements in flow-meters by using longitudinally grooved mandrels to produce a fluted internal configuration for centering the floating indicator.

Machines for producing precision bore tubing by a continuous process have been described by Everett[7] and Stong[8]. With increasingly new applications, the continuous process is to be desired, both from a production and economical view.

Growing demands for precision bore tubing have led manufacturers to stock a complete range of sizes in Pyrex (7740) glass. These readily accessible sources are providing precision tubing to the glass shops and laboratories in much the same manner as metal drill rod and precision ground stock is available to the machine shops.

Numerous descriptions have been given in the patent literature for forming softened glass tubing over metal mandrels without the aid of vacuum. These methods will not be reviewed because the process does not maintain close dimensional tolerances and eventually alters the forming mandrel by oxidation.

## Vacuum Forming on the Glass Lathe

An ideal laboratory or small glass shop set-up, which is effective and easily controlled, is illustrated in Figure 1. The materials and equipment required consist of a mandrel having the desired shape or dimensions, a mechanical vacuum pump, gas or other heating means, glass tubing, vacuum swivel and glass lathe. These will

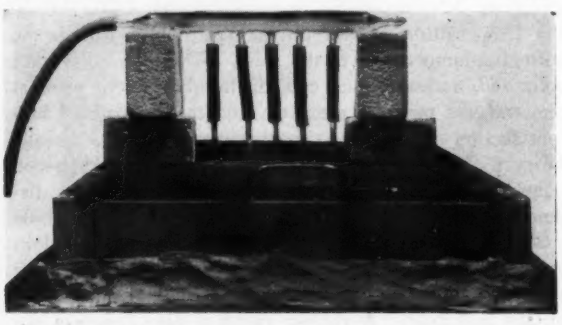

**Fig. 2. Oven shrinking involves little skill and high production without expensive machinery. The glass manifold, with mandrels, may be removed from the hot oven for inspection or reloading.**

be individually treated in detail later in the article.

The glass tubing, containing the mandrel, is secured in the lathe chucks as shown. Rubber hose connects the tube's open end with a vacuum swivel to form a closed vacuum circuit to the mechanical pump.

While the glass rotates in the lathe, the vacuum is checked with a high frequency spark coil on a section of glass tubing placed in the vacuum hose line. Fluorescence of the internal glass wall without glow discharge is evidence of the proper vacuum. The gas-air ribbon burner is ignited and the entire mandrel, within the evacuated glass tubing, is heated just below the glass' collapsing temperature. (The ribbon burner also prevents mandrel warping due to uneven heating.) A gas-air hand burner flame is then applied to the mandrel end farthest from the vacuum source. As the glass tube commences to shrink about the mandrel, an obvious visual change occurs. The dull red glow of the mandrel, the change in light reflection off of the tube, and the apparent circular line of contact where the glass first touches the mandrel indicate to the operator the rate at which shrinking takes place. The travel of the hand operated shrinking burner is adjusted to correspond with these visual aids.

After the shrinking has been completed, the mandrel, still in the evacuated glass tube, is brought to a uniform red heat by increasing the ribbon burner flame size. Overall uniform heating, in this manner, minimizes longitudinal temperature gradients with resulting elimination of hard strains at room temperature. If bowing of small diameter mandrels occur, the lathe tail stock is slightly retracted to assure straightness of the tube. When the tubes are cool enough to be handled, the mandrels are removed and the precision glass tubing is oven annealed in a vertical position.

Mandrels which resist removal are loosened by cooling in liquid nitrogen and removed before the parts regain room temperature. The tubes are cleaned with 5 per cent hydrofluoric acid solution to remove traces of graphite and are immediately rinsed in running water.

### Oven Shrinking

A seldom used but effective production technique which requires no machinery is the oven shrinking process. The mandrel is placed within a closed end glass tube, the tube evacuated and flamed (to drive off moisture) and then tipped-off just above the mandrel. The evacuated tube end is placed in a shallow container of sand so as to support the tube in a vertical position and then placed in a high temperature oven. The shrinking temperatures should be set at 25° C less than the softening temperature of the glass. When the tubes have collapsed, annealed, and cooled, the glass is cut open at one end, the mandrel removed, and the sand pitted bottom section cut off. An improvement in this technique (Figure 2) provides the oven top with equally spaced holes. A glass manifold is constructed so that the distance between the tubulations corresponds to the hole spacings in the oven top. The mandrels are placed in long narrow test tubes and the open end of each tube is sealed or connected by rubber tubing to the tubulations on the manifold. A rubber vacuum hose connects the fore pump to the main trunk of the manifold. The length of this hose should be sufficient to allow for easy removal of the manifold and tubes when necessary for visual inspection as the operation proceeds. The vacuum is maintained in the system until the glass shrinks, anneals, and cools within the oven. No sand is necessary, but the mandrels must extend slightly above the oven top to provide support for the softened glass. By this inexpensive method, unskilled workers can produce large quantities of precision tubing.

### Heating Means

Many heating methods have been used, such as indirect heating through carbon, steel and ceramic materials, electric resistance heating, R.F. induction heating, radiant gas burners, and a variety of other gas type burners. Any source of uniform heat capable of attaining the glass shrinking temperature is acceptable.

### Mandrels

The mandrel is made of a material which will not deform at glass softening temperatures, is readily machinable, and has low vapor pressures. Low carbon steel, drill rods, and stainless steel are commonly used with soft and hard glasses, while carbon, molybdenum, and tungsten mandrels are used with fused quartz and Vycor (Figure 3). Metal mandrels containing zinc, cadmium, or brazed parts should not be used. Special size mandrels, not available in standard drill rods, should be centerless ground specifying tolerances of $\pm$ 0.0002 in. for precision work, be free of scratches, and straight (minimum camber). It is essential that the mandrels be packaged before storing to retain their precision (see Figure 4). Sharp edges on glass tubing will scratch the mandrel surface. Careful insertion and removal of mandrels, as well as fire polishing the glass tubing ends, will prevent surface damage. The weight of solid mandrels becomes appreciable as the diameter increases, producing heating, holding, and cooling problems. Mandrels of metal tubing are preferred, when available, because rapid shrinking and uniform heating is possible. With a rise in temperature, the diameter of the mandrel will increase because of thermal expansion. This growth in size at elevated temperatures must be compensated for by starting with a mandrel smaller in diameter than the required tube bore.

The diameter of the mandrel at room temperature is related to the finished inside diameter of the tubing as follows:

$$D_m = D_g \frac{1 + a_g T}{1 + a_m T}$$

in which —T is the temperature rise from room temperature to the collapsing temp.

$a_g$ is the linear coefficient of thermal expansion of the glass.

$a_m$ is the linear coefficient of thermal expansion of the mandrel material.

Both $a_g$ and $a_m$ can normally be obtained from handbooks for the materials used. (Evacuated tubes collapse, when heated, to approximately 100° C below their softening temperature. This varies with the type of glass and tubing diameter used.

Several procedures are employed by manufacturers of precision bore tubing to effect small changes in the final tube tolerances. Madden and Kramer[9] adjust shrinking temperatures so as to obtain smaller or larger inside diameters by the respective use of cold or hot shrinking

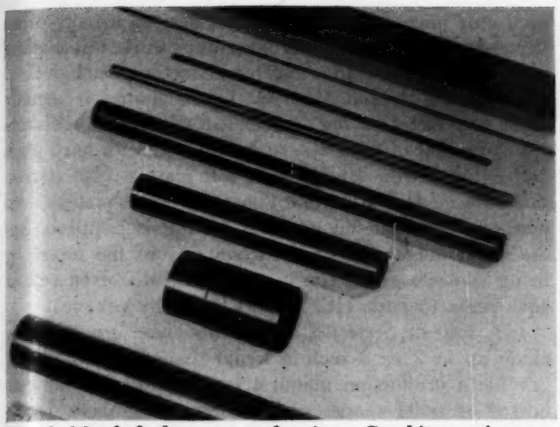

**Fig. 3. Mandrels for vacuum forming. Graphite coating prevents glass adhesion at high temperatures. Carbon boats and tungsten rod (upper part of photo) used for shrinking quartz and Vycor.**

temperatures. Graver and Conway[10] suggest mandrel removal prior to annealing for easy mandrel removal, final size control, and stabilizing the glass tubing.

Mandrels may be typed in five categories: (1) Coated; (2) Uncoated; (3) Dissolve out; (4) Split, and (5) Compound.

(1) *Coated Mandrels*—To facilitate the easy removal of straight sided or tapered mandrels, a firm adherent coating of colloidal graphite is applied to the mandrel in the following manner:

(A) Clean Mandrels

(1) Degrease in trichlorethylene.

(B) Graphite Dip

(1) Heat mandrels to 300° F.

(2) Dip into dilute Aquadag* solution—20 parts by volume distilled water—1 part by volume Aquadag.

(3) Redip mandrel when dry (optional).

(C) Bake

(1) 600° F. for one hour. When cool, remove and burnish with a dry soft cloth to obtain a black mirror finish. The extremely thin coating does not affect the mandrel's dimension. When the coating is damaged and the mandrel metal visible, a new coat of carbon should be applied as before.

*Aquadag—Acheson Colloids Company, Port Huron, Michigan.

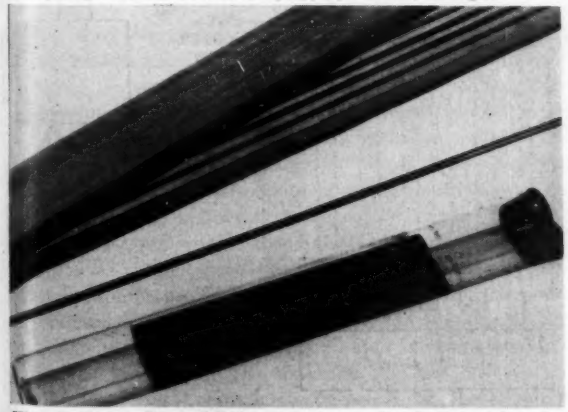

**Fig. 4. Grooved wooden boxes or paper lined glass tubes are used as storage containers to retain the mandrels scratch free surface and eliminates bending.**

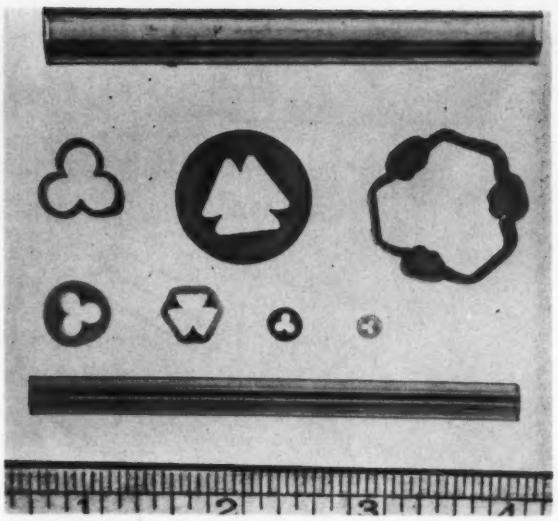

**Fig. 5. Three point supports formed from compound mandrels. Upper row, of cross sections, are bearing surfaces for movable shafts operated in vacuum. Lower row, clover leaf patterns that support helices in electronic tubes.**

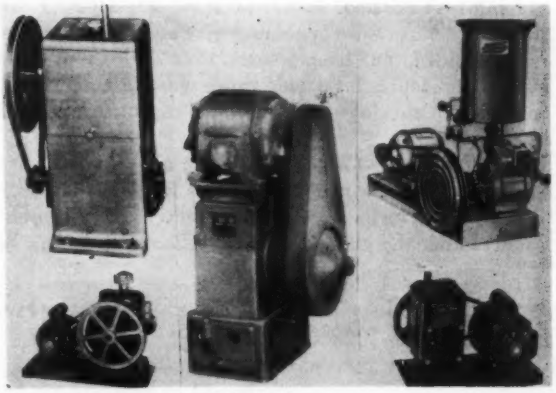

**Fig. 6. A variety of mechanical vacuum pumps are commercially available. Those having a high pumping speed are desirable for vacuum forming.**

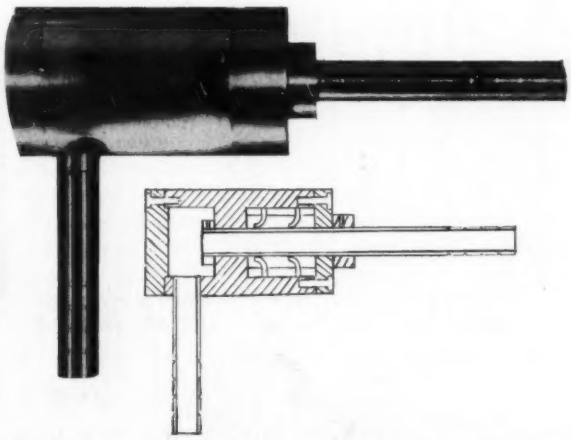

**Fig. 7. Vacuum swivels, which use tight fitting rubber washers, effectively maintain the internal vacuum during shaft rotation.**

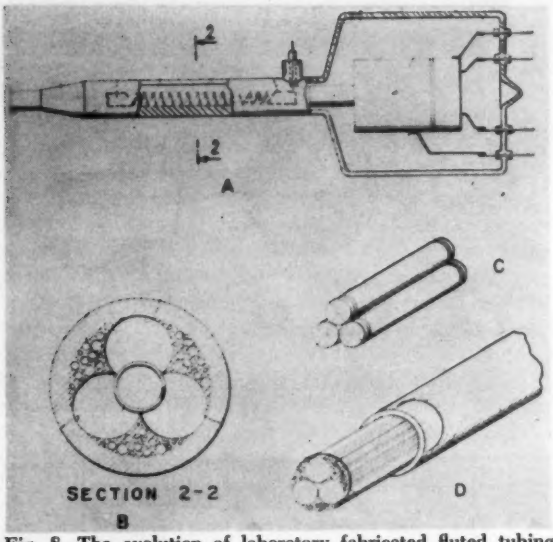


**Fig. 8. The evolution of laboratory fabricated fluted tubing. The partial cross section of the microwave tube at top shows the helix axially supported by the percision tubing.**

(2) *Uncoated Mandrels* (excluding carbon and graphite)—Uncoated mandrels may be used if the shrinking temperature is not excessive and a high vacuum is maintained, i.e. temperatures over 750° C. or light mandrel oxidation invariably cause glass to mandrel adherence or 'sticking' which results in fracture of the glass parts.

(3) *Dissolve Out Mandrels*—These are required when the geometry of the mandrel presents irregularities, such as depressions or undercuts, which prevent the mandrels' removal after the glass is shrunk. The mandrels can be used only once, but the advantages derived usually offset the cost. For small quantity laboratory work, this method is less expensive than a machined sectional mandrel as described in Method 4 below. The mandrel is usually made of a metal having a coefficient of expansion closely matching that of the glass, such as Kovar with hard glass and Sylvania No. 4 alloy with soft glasses. No corrections are made for thermal expansion when matched expansions exist and no graphite coating is required, but the usual outgassing or decarbonizing of the metal by firing is necessary. The mandrels are dissolved out in aqua regia (3 parts HCl, 1 part $HNO_3$ by volume).

(4) *Split or Sectional Mandrels*—These are normally made up in 2 or 3 section wedge-shaped pieces. They provide a production mandrel for forming internal embossed or relief shapes such as letters, numbers, trademarks, and protrusions on precision bore tubing. The latter may be used for sealing side arms or lead wires without distorting the accurate bore. The tapered wedges are milled, alignment pins and countersunk end holding screws provided, and the entire assembly is given a final finish in the lathe or grinder. All sharp edges should be rounded and corners given a slight radius. These assemblies are best made of stainless steel with end holding screws of the same material. After shrinking, the glass is scored with a file on both ends just inside the screws. When the glass is snapped off, the screws and mandrels sections can be easily removed and reused. Diameters less than one-quarter inch do not lend themselves to this method. When constrictions or necking-down is required on a precision bore tube, a two piece mandrel is used that must be removed from both ends of the tube. A mandrel of this type is described by Thorough[9].

(5) *Compound Mandrels*—These are groupings of in-

(*Continued on page* 351)

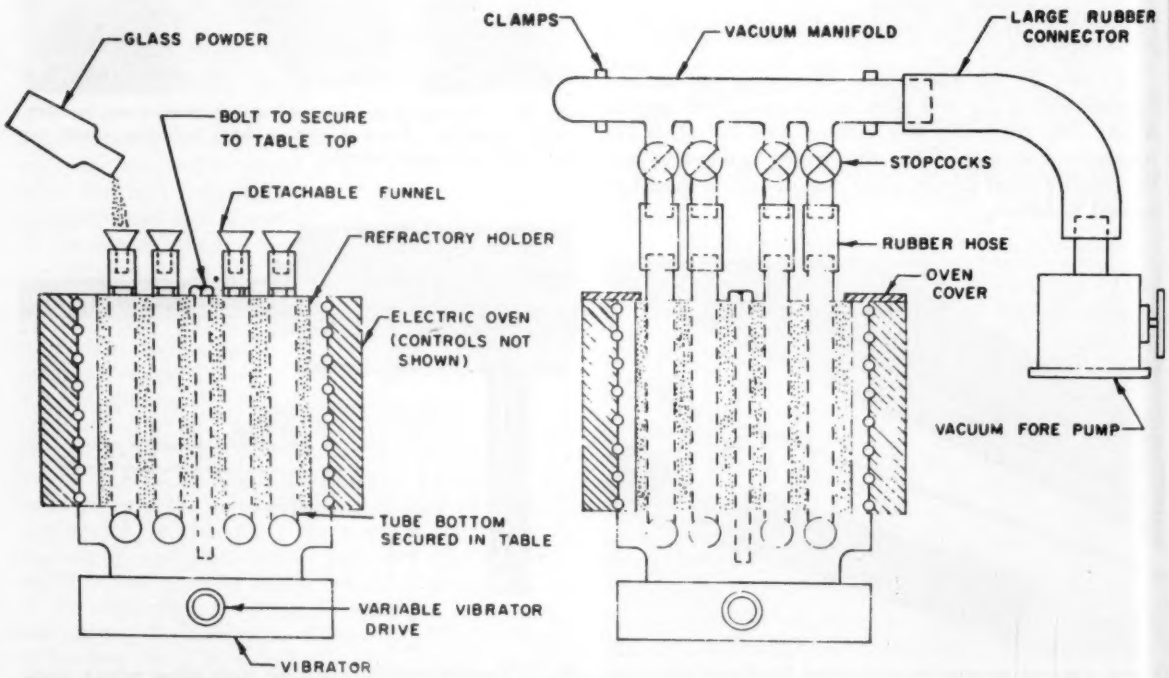


**Fig. 9. In the apparatus shown, vibration, heat, and vacuum combine to produce transparent tubing when glass powder is used as the filler for irregular surface mandrels.**

# Acid-Base Relationship in Glass Systems

## A NEW ACID-BASE CONCEPT APPLICABLE TO AQUEOUS SYSTEMS, FUSED SALTS, GLASSES, AND SOLIDS

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**PART II**

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### III. ACIDITY OF GLASSES

Whenever a scientist is confronted with a new phenomenon such as an unexpected chemical reaction or a new physical property, it is well worthwhile for him to examine how this property changes with the temperature. Thus one may expect to obtain deeper insight into the true nature of acidity if one could examine its manifestations over a wider temperature region. For obvious reasons our most widely used instruments for measuring acidity work only over a rather narrow temperature region. This experimental limitation, however, should not prevent us from looking for other signs even if they are only of a qualitative nature which can tell us something about the change of the acidity of a substance with temperature. L. F. Audrieth and Therald Moeller[9] reached the same conclusion when they wrote: ". . . even today, in spite of the development of the Broensted point of view and the broader and more inclusive Lewis representation, our scientific thinking along these lines has been limited largely to phenomena and observations over a rather narrow temperature range."

From the screening viewpoint we must expect that the acidity of a compound changes with temperature. The boron atom must have a very high screening demand. Elemental boron begins to volatilize only in the electric arc and the extent to which the vapor contains atoms is not well known. In the molecule $BF_3$ the $B^{3+}$ core is neutralized but incompletely screened by three anions of low polarizability. The arrangement of the three anions in a plane does not provide sufficient screening in space for the $B^{3+}$ core and, as a result, $BF_3$ is an acid. Like other acid catalysts $BF_3$ can initiate the polymerization of olefins.

We are accustomed to think of the rate of chemical reactions as increasing with increasing temperature. This rule, however, cannot be valid if a reaction is catalyzed by a molecule such as $BF_3$, the acidity of which increases with decreasing temperature. R. M. Thomas and associates[10] found that the polymerization of isobutylene requires considerable time when carried out at $-9°C$ using $BF_3$ as a catalyst. However, at $-80°C$ the polymerization is much faster and leads to larger molecules. They also found that lowering the reaction temperature from $-10°C$ to $-90°C$ increases the average molecular weight of the polymer from 10,000 to 200,000.

These data show how the absolute acidity of $BF_3$ increases with decreasing temperature. For chemical reactions which involve acids and bases this relation becomes blurred because the acidity of all substances changes with temperature. Chemical technologies offer many examples of high temperature reactions resembling salt formation.

The formation of portland cement clinker; the melting of silicate, borate, and other glasses, glazes, and enamels; the reactions of fused glasses and slags with the refractory lining of the furnaces—all of these reactions and many more can be treated as acid-base reactions.

It became customary to classify the oxides which are involved in these reactions into basic, acidic and amphoteric oxides primarily on the basis of their interaction with water at room temperature. $SiO_2$, $B_2O_3$ and $P_2O_5$ were considered to be acids and the oxides of the alkali and alkaline earth metals were called bases. Some oxides, e.g., $Al_2O_3$, $Fe_2O_3$ and ZnO, exhibit intermediate properties and, consequently, they were called amphoteric. Today, one may consider this approach to the high temperature chemistry of oxides rather naive but until not too long ago chemistry was limited to gases and liquids and, among liquids, the majority of the factual knowledge pertained to aqueous systems. At a time when glass melting and ceramic processes, our oldest chemical technologies, were brought onto a scientific basis, aqueous chemistry was the closest field which

was available for comparison. As one might expect, this comparison with aqueous systems led to serious difficulties. Nearly thirty years ago, N. Kreidl[11] in a paper on "Basic Oxides and Properties of Glasses" pointed out some of the more obvious inconsistencies in the relations between composition and properties of glasses and he suggested, for example, that MgO be treated as an acid. One of the discussers of his paper made a typical comment, namely, that he would go along with the speaker to bracket $Al_2O_3$ and ZnO as acids but not MgO. This discussion remark shows the difficulty of a chemist to abstract himself from aqueous chemistry and approach a new subject with an open mind.

Chemists are well aware that crucibles made of fused silica are not suitable for melting alkali carbonates. Silica is an acid which reacts with fused $Na_2CO_3$ under salt formation: alkali silicate. Silica dishes, however, are attacked not only by alkalies but also by hot concentrated phosphoric acid. In this reaction silica behaves as a base. The structure of the reaction product, silicyl phosphate, indicates that the $P^{5+}$ ion dominates the geometry of the lattice. The $P^{5+}$ ion is screened by four tetrahedrally arranged $O^{2-}$ ions in close proximity and it has forced the weaker $Si^{4+}$ ion into a position where it is surrounded by six $O^{2-}$ ions at greater distances. If we want to bracket the corrosion of the silica dish by phosphoric acid as an acid-base reaction, $P_2O_5$ must be called the acidic and $SiO_2$ the basic oxide. We can rely on the crystal structure for identification of the acid-base character of the constituents.

In a similar fashion we can use the structure of calcium metasilicate to show that silica is an acid which in a polymerized form—in this case as rings of $SiO_4$ tetrahedra—contains the $Ca^{2+}$ ion in a position of higher coordination, i.e., surrounded by anions at greater distances. Also in orthosilicates the metal ions, as a rule, occupy positions of higher coordination and the acidic elements are isolated $SiO_4$ tetrahedra, i.e., $SiO_4$ tetrahedra which do not have to share $O^{2-}$ ions. We can understand these structures and the reactions which lead to orthosilicates by assuming that the $Si^{4+}$ ions of silica have improved their screening by surrounding themselves with $O^{2-}$ ions of greater polarizability. The $O^{2-}$ ions of silica have a very low polarizability because they are exposed to two $Si^{4+}$ ions each. CaO provides more polarizable $O^{2-}$ ions and in the orthosilicate structure the $Si^{4+}$ ions are surrounded by four $O^{2-}$ ions, the excess charges of which are neutralized by $Ca^{2+}$ ions and not by other silicons. This interpretation of the reaction between CaO and $SiO_2$ in the orthosilicate seems to justify the use of the acid-base concept in high temperature chemistry.

Unfortunately, the existence of the compound $3\ CaO \cdot SiO_2$ disturbs this simple picture. How can an acid react beyond the ortho stage? What is the driving force for calcium orthosilicate to react with an additional mol of CaO?

These questions show that even in simple binary systems we meet with considerable obstacles if we want to explain the chemical reaction between $SiO_2$ and CaO on the basis of salt formation alone. Before we return to this problem we shall follow another line of thought and examine the extent the formation of alkali silicate glasses can be understood on the basis of salt formation.

In recent years the concept of "acidic constitutents" of glasses has been replaced by the concept of "network formers" and the formerly "basic" oxides are now called "network modifiers." The use of the acid-base concept goes far back in glass technology because it became associated with two of the most important properties of fused silicates, namely, their chemical resistivity and their tendency to form glasses rather than to devitrify. The pure $SiO_2$ would make the ideal glass in many respects were it not for its very high melting temperature. Basic oxides lower the melting temperature but, unfortunately, they make the glass more susceptible to corrosion by water and to devitrification.

These limitations explain why our modern window glass has a chemical composition which is not so very different from ancient Egyptian glass beads. The glass melters had to compromise between meltability, chemical resistivity and devitrification. This compromise leaves only a relatively small composition field in the ternary system silica-alkali-lime. By experience the glass melter learned that a batch which contained too much sand did not melt properly, one which contained too much lime did not form a clear glass but partly crystallized or devitrified on cooling, and one which contained too much alkali produced a glass which was not stable. Such a glass soon develops a "haze" by reacting with the water of the atmosphere.

The first scientists who became interested in the chemical properties of glass were physicists who experimented in the field of optics and who neded glasses with different optical properties and fairly good chemical resistivities. As early as 1817-19 Joseph von Fraunhofer[12] studied the development of "haze" on glasses of simple and widely varied compositions and he succeeded in developing means to prevent the "hazing" of glass. This work in its simplicity and clear perception answers most of the questions which are pertinent to the problem of chemical resistivity. J. von Fraunhofer's work was published only much later. It may be called the classical paper on the atmospheric corrosion of glass and its prevention. His method of improving the glass surface, namely, by washing it with a diluted sulfuric acid in order to remove some of the alkalies, is still used, at least in principle.

From the viewpoint of the acidity concept as applied to glasses, the following findings of J. von Fraunhofer are pertinent to our problem:

(1) Potassium silicate glasses deteriorate faster than the corresponding sodium silicates.

(2) Increasing the silica to alkali ratio improves the chemical resistivity to a certain extent but the introduction of lime into these glasses is far more effective than increasing silica.

(3) The accidental impurities, in particular iron and alumina, which these glasses dissolve from the melting pot are most effective in improving the chemical resistivity. They give noticeable improvements even in small concentrations.

It is not surprising that the chemical resistivity of an alkali silicate increases with increasing acidity because, in contrast to the easily soluble alkali, the acid itself is insoluble in water. Amazing, however, is the fact that even a highly acidic glass, e.g., one containing 85 per cent silica and 15 per cent $K_2O$, is still susceptible to

the attack by water, whereas the replacement of, say 15 per cent, $SiO_2$ by the water soluble CaO produces a stable glass. This paradoxical phenomenon must be understood if our approach to the constitution of glasses is correct.

We may state this problem differently. The chemical resistivity of an alkali silicate glass seems to be a function of its acidity. For a given alkali the chemical resistivity increases with increasing concentration of silica. For a given alkali to silica ratio the chemical resistivity decreases with increasing basicity of the alkali. A glass of the composition 1 mol $Li_2O$ and 3 mols silica is fairly stable, the corresponding sodium glass deteriorates within days and the potash glass becomes hazy and sticky within a few hours. If this relation between the chemical resistivity of a glass and its acidity holds true, we are forced to conclude that in certain composition fields calcium oxide functions as a stronger acid than silica because replacing some of the silica by CaO can improve the chemical resistivity of an alkali silicate. A pure sodium silicate containing 85 per cent $SiO_2$ would be useless as a window pane but replacing 15 per cent of the silica by 15 per cent CaO gives a glass which would be satisfactory. What is the structural explanation of this paradoxical phenomenon?

Such an atomistic or structural explanation has to answer two pertinent questions. Firstly, why does an increase in the acidity of an alkali silicate glass decrease the rate of its reaction with water or acids? Secondly, how does the introduction of CaO, MgO, and similar oxides into an alkali silicate glass change it in the direction toward greater acidity?

It is important for us to realize that the first question we have to answer involves a rate problem because no alkali silicate is in equilibrium with water or diluted acid, but it will hydrolyze if given sufficient time. The fact that sodium silicates dissolve within a few hours but soda lime silicates have survived exposure to the atmosphere and water for centuries indicates only that the rate of hydrolysis varies with the composition. The second question concerning the effect of CaO and similar oxides upon the acidity of a glass makes it desirable to measure the "acidity" of glasses by several methods so that one does not depend on the chemical resistivity alone as an indication of its acidity.

## IV. MEASUREMENTS OF ACIDITY AT HIGH TEMPERATURE

With respect to the acidity of a system we learned that the proton is not very different from other cations which have a strong screening demand. The proton, however, is unique with respect to the possibilities of measuring the acidity of a system because protons, the only cations without electrons, can easily migrate through solids. During chemical reactions protons do not appear in a free or hydrated state but are always screened by the electron clouds of anions. This feature is utilized in the glass electrode where a glass membrane separates a liquid of known acidity from the unknown. The medium which has the highest acidity or the least screening power for protons will lose some protons because the protons tend to migrate through the permeable membrane into the liquid which is the better screener. The driving force for this diffusion process is the tendency to equalize the screening of the protons in both systems. The anions, however, cannot follow the protons through the membrane and, as a result, an electrical potential is established which counteracts the diffusion of protons. This potential difference between the known and the unknown liquid can be measured and serves as an indicator of the acidity or basicity of the unknown.

The glass electrode measures the difference in the degree of screening of protons which exists between the two liquids. It is most important to realize that the degree to which protons are screened depends on the system as a whole, and not only upon the concentration of protons. For this reason there can be no rigorous relation between the concentration of hydrogen ions in the two solutions and the potential difference between them. It is well established that the addition of neutral salts, e.g., LiCl and KCl, affects the pH of a diluted acid to a certain extent. Additions of neutral salts to an acid may have strong effects upon its catalytic action with respect to hydrolyzing an ester without changing the actual concentration of hydrogen ions. We do well to remember what M. Dole[13], one of the pioneers in the field of the glass electrode, once wrote: "We do not know what we measure when we measure pH but we do know that it is very important. We correlate the pH values with the observable properties of the solution, thus giving our pH data practical significance."

The counterpart of the pH measurement is the contact potential between metals and semiconductors, i.e., between systems which contain free electrons as anions. The free electron is the only anion which does not have a positive core and, as a result, it can move freely from one system to another. The less screened system will attract electrons from the better screened system until this trend to equalize the screening of both systems is counteracted by the potential difference which it causes. The thermo power of a combination of two solids is a measure of the difference in the screening demands of the two solids as a function of the temperature. The absolute screening demand is more difficult to measure because it is strongly affected by adsorbed gases and impurities. The measurements of contact potentials are difficult experimentally so that only few reliable data are available.

Systems which contain neither protons nor free electrons are difficult to evaluate with respect to their screening demand or their acidity. As no direct methods exist one has to look for indirect methods. Some of these methods which permit us to estimate the acidity of fused salts and glasses shall now be discussed.

### (1) Optical Indicators of the Acidity of Glasses

Nearly 50 years ago W. L. Bruner[14] suggested the use of chromium oxide as an indicator for determining the acidity of lead glazes. He found that under oxidizing conditions chromium produces a red crystalline chromate of the formula $2\ PbO \cdot CrO_3$ when the glaze is "basic." In "acidic" lead glazes a yellow crystal is formed which had the formula $PbCrO_4$. He suggested transition from red to yellow for testing the acid-base character of lead glazes just as one uses the color change of organic indicators for determining the acidity-basicity of aqueous solutions.

W. D. Bancroft and R. L. Nugent[15] suggested a different method for estimating the acidity of fused salts and glasses. Some elements are stable in different states of oxidation, depending upon the acidity of the environment. This relationship was used by W. L. Bancroft and R. L. Nugent to estimate the acidity of borate and phosphate glasses by means of manganese. The nearly colorless $Mn^{2+}$ ion which is stable in acidic melts changes into the deep purple $Mn^{3+}$ ion if the basicity of the melt is increased.

W. A. Weyl and E. Thümen[16] developed a quantitative method which was based on the same principle of valence change but using chromium oxide as the color indicator. For a constant temperature and a constant atmosphere, e.g., air, the equilibrium between the green chromic ion and the yellow chromate ion depends upon the acidity of the melt. Acid melts favor the lower state of oxidation, more alkaline melts favor the higher state of oxidation. Metaphosphoric acid, for example, produces a pure green glass with $Cr_2O_3$ which does not contain any chromate. This relation which holds true in a rather general way for many elements indicates that for a given temperature the chromium core $Cr^{6+}$ can be screened in two ways, either by four $O^{2-}$ ions in close proximity so that they can be strongly deformed or by three electrons and a larger number of $O^{2-}$ ions at greater distances. The electronic structure of the chromium core is interpenetrable for electrons so that the $Cr^{6+}$ core is best screened when surrounded by ions which permit electronic interpenetration, i.e., by polarizable anions. In an acidic environment, i.e., in a glass where the $O^{2-}$ ions are already tightened by strong cations, the chromium core is better screened by electrons and, consequently, the equilibrium is shifted toward $Cr^{3+}$ ions:

$$2\,Cr^{6+} + 3\,O^{2-} = 2\,Cr^{3+} + 3\,O\,.$$

As the acidity of the environment increases and the $O^{2-}$ ions become less polarizable, the chromium core cannot be properly screened by an environment of $O^{2-}$ ions and, as a result, it attracts electrons and changes into a $Cr^{3+}$ ion. The same process takes place if the temperature is raised because increasing the thermal vibration also interferes with the mutual interaction of the $Cr^{6+}$ core with its anions. For this reason the temperature has to be kept constant in order to use the $Cr^{6+}$ — $Cr^{3+}$ equilibrium or similar equilibria for comparing the acidity of different melts.

The above equation shows that the valance change of the chromium is accompanied by the evolution of oxygen. As a result, the equilibrium depends upon the partial oxygen pressure over the melt and the latter also has to be kept constant.

Several elements behave very much like manganese and chromium, but the oxidation equilibrium between the green $Cr^{3+}$ and the yellow $Cr^{6+}$ ion is particularly suitable for studying the acidity of glasses because the trivalent chromium has an absorption band in the orange part of the spectrum (650 mμ) where chromates do not absorb. W. A. Weyl and E. Thümen[16] used this couple to show that potassium glasses are more basic than sodium glasses of the same molecular ratio. Later W. Stegmaier and A. Dietzel[17] extended this work to other acid-base indicators and found very interesting relations between compositions of binary melts such as alkali borates, phosphates, etc., and their respective acidities. These experiments are straightforward and require little explanation. The difficulties which one has to face in order to extend this work to other glasses besides silicates are of an experimental nature. Establishing true equilibria with the atmosphere for glasses of widely different compositions and widely different viscosities is time consuming because in order to be meaningful the measurements had to be made at a certain constant temperature. Table II gives some of their results.

**TABLE II**

Alkali Concentration (mol. per cent) which Produces Color Changes in Various Indicators Present in Molten Glasses

| Glass | Indicator $Cr^{3+}$—$Cr^{6+}$ % | $V^{3+}$—$V^{5+}$ % | $Mn^{2+}$—$Mn^{6+}$ % | $Fe_2O_4$ % |
|---|---|---|---|---|
| $Na_2O$–$SiO_2$ | ~15 | ~15 | 67 | — |
| $K_2O$–$SiO_2$ | — | — | 42 | — |
| $Li_2O$–$B_2O_3$ | — | — | — | 17 |
| $Na_2O$–$B_2O_3$ | 36 | 38 | 64 | 12 |
| $K_2O$–$B_2O_3$ | 15 | 24 | 50 | 8 |
| $Na_2O$–$P_2O_5$ | 65 | 53 | — | — |
| $K_2O$–$P_2O_5$ | 46 | 47 | 63 | — |

H. Lux and E. Rogler[18] used the $Cr^{3+}$ — $Cr^{6+}$ indicator in order to determine the acidity of ternary borate melts.

Very acid melts, e.g., fused boric acid, which contain a small amount of alkali (anhydrous pure $B_2O_3$ does not dissolve $Cr_2O_3$ or other oxides of tri- and divalent elements) dissolve $Cr_2O_3$ and show the green color of the chrom ion. Basic melts form the yellow chromates. A sodium borate of a composition which produces a mixture of $Cr^{6+}$ and $Cr^{3+}$ (endpoint of titration) was chosen as the "neutral" melt. It should be repeated here that such a "neutral" melt is much more basic than neutral water, the reference point of aqueous and acid-base relations. H. Lux and E. Rogler reasoned as follows: If a third oxide is added to such a "neutral" melt it can remain neutral only if the oxide is neither a base nor an acid; in other words, the addition of neutral oxides will not affect the color of this melt. Acidic oxides will change the color toward green, basic oxides toward yellow. It should be inserted here that this postulate is not rigorously correct for aqueous solutions. Neutral mannitol added to a weakly acid solution of boric acid increases the acidity.

Based on the color change green ($Cr^{3+}$) — yellow ($Cr^{6+}$) H. Lux and E. Rogler found that the neutral point (N.P.) for the binary system $Na_2O$ —$B_2O_3$ corresponded to a melt containing 17.5 mol per cent $Na_2O$ corresponding to the formula $Na_2O$, 4.7 $B_2O_3$. When this binary system is changed into a ternary one by adding an oxide X the N.P. will be shifted in a way which can best be described by following several cases.

(1) The oxide X has the same acidity as $B_2O_3$. In this case those ternary compositions will be neutral which correspond to line I in the diagram (Fig. 1a) be-

cause this line represents compositions for which the ratio $Na_2O$ to $(B_2O_3 + X)$ is constant.

(2) The oxide X is neutral and acts just as a diluent. In this case the N.P. of the ternary melts is determined by the $Na_2O$ to $B_2O_3$ ratio only and the neutral ternary melts correspond to the line II (Fig. 1a).

(3) The oxide X is basic and has the same base strength as $Na_2O$. The neutral melts are then represented by the line III which corresponds to a constant ratio $(Na_2O + X)$ to $B_2O_3$ (Fig. 1a).

These lines I, II and III divide the ternary field into four fields A-D which have the following signficances. A shift of the N.P. into the field.

A means that X is a stronger base than $Na_2O$.

B means that X is a weaker base than $Na_2O$.

C means that X is a weaker acid than $B_2O_3$, and

D means that X is a stronger acid than $B_2O_3$.

When $K_2O$ is substituted for $Na_2O$ the N.P. curve moves into the field A as one would expect because $K_2O$ should be a stronger base than $Na_2O$. Indeed, complete replacement of $Na_2O$ by $K_2O$ gives a strongly basic melt and neutrality can be restored by decreasing the $K_2O$ concentration to 8 mol per cent as compared with 17.5 mol per cent $Na_2O$. Complete replacement of $Na_2O$ by $Li_2O$ produces a more acidic melt and, in this case, the alkali concentration has to be raised to 46 mol per cent in order to restore neutrality. As long as one examines binary alkali borates the acidity-basicity relations conform with expectations. However, as soon as one departs from the binary systems the situation becomes more complex. Replacing a part of the sodium ions by lithium ions shifts the N.P. into the field D and only if a considerable percentage of $Li_2O$ is substituted for $Na_2O$ does the curve turn and move through the field C into B (Fig. 1b). This course of the N.P. curve means that the first substitution of $Li_2O$ increases the acidity in a way which makes $Li_2O$ a stronger acid than $B_2O_3$. A similar situation was found to occur when BeO or MgO was introduced, but it was most pronounced for BaO and PbO. Among the oxides of trivalent elements that of lanthanum is the most acidic and it has a much stronger effect than aluminum oxide. Ordinarily, in low temperature chemistry, $La_2O_3$ is considered rather "basic," as it is the only oxide of the formula $Me_2O_3$ which can absorb and combine with $CO_2$ from the atmosphere.

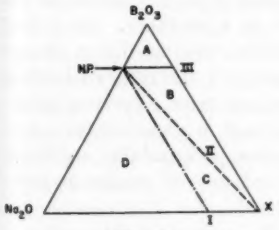


Fig. 1a

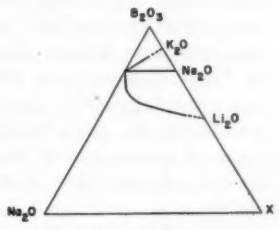


Fig. 1b

$$\text{I} \quad \text{——} \cdot \text{——} \quad \frac{Na_2O}{B_2O_3 + X} = \text{Constant}$$

$$\text{II} \quad \text{— — — —} \quad \frac{Na_2O}{B_2O_3} = \text{Constant}$$

$$\text{III} \quad \text{————} \quad \frac{Na_2O + X}{B_2O_3} = \text{Constant}$$

Fig. 1

H. Lux and E. Rogler attempt to explain this apparently paradoxical behavior on the basis of the stabilization of certain borate ions. It is likely that the presence of a third oxide affects the coordination number of the boron. However, we have to look for another explanation because we find the same situation in silicate glasses where a change of the coordination of the $Si^{4+}$ ions is less likely to occur.

The experiments of H. Lux and E. Rogler based on color indicators confirm for alkali borate what the chemical resistivity revealed for alkali silicates: MgO, CaO, BaO, etc., are acids and they show a stronger acidity when introduced into these melts than $B_2O_3$ or $SiO_2$.

### (2) Stability of Isopolyacids in Fused Salts

About ten years ago H. Flood and T. Förland[19] started an experimental program with the aim to determine the acidity and basicity of fused salts which contained $O^{2-}$ ions and complex anions of oxyacids, e.g., carbonates, borates and sulfates. $O^{2-}$ ions are stable only when exposed to positive fields of sufficient strength to prevent the dissociation of the $O^{2-}$ ions into $O^-$ ions and electrons. In combination with weak cations the $O^{2-}$ ions change into $(O_2)^{2-}$ and $(O_2)^-$ ions. Consequently, one has to assume that in a system of oxides or salts of oxyacids all $O^{2-}$ ions are polarized. The degree to which they are tightened must depend on the nature of the polarizing cation, their charges, sizes and electronic structures. According to H. Flood and T. Förland, the characteristic process of acid-base reaction is the transfer of an $O^{2-}$ ion from one state of polarization to another (Section II, 2).

In silicates the acid-base transition consists of the breaking of an oxygen bridge (strongly polarized $O^{2-}$ ion) and the formation of a pair of less polarized non-bridging $O^{2-}$ ions:

$$(O^{2-})_3\ Si^{4+}\ O^{2-}\ Si^{4+}\ (O^{2-})_3 + O^{2-} = 2\,[\,(O^{2-})_3\ Si^{4+}\ O^{2-}\,].$$

This process connects acid-base reactions with the disintegration of macromolecules through changing bridging $O^{2-}$ ions into non-bridging $O^{2-}$ ions. The bridging $O^{2-}$ ions which are exposed to two $Si^{4+}$ ions are more polarized and, therefore, less polarizable than the non-bridging ones.

Experiments concerning the stability of the pyrosulfate ion $(S_2O_7)^{2-}$

$$\begin{array}{ccccc} & & O^{2-} & & O^{2-} \\ O^{2-} & & S^{6+} & O^{2-} & S^{6+} & O^{2-} \\ & & O^{2-} & & O^{2-} \end{array}$$

in fused salts reveal that the bridges are broken through the polarizing action of the cations. $K^+$ ions are less effective than $Na^+$ ions and the small $Li^+$ ions are the most effective ones in changing pyrosulfate into sulfate and sulfur trioxide, according to

$$(S_2O_7)^{2-} = (SO_4)^{2-} + SO_3.$$

Just as the "acidity" increases with increasing field strength, i.e., from $K^+$ to $Li^+$, it also increases when going from a noble gas-type ion to one with 18 outer electrons. Potassium pyrosulfate was found to be more stable than thallous pyrosulfate and sodium pyrosulfate more stable than silver pyrosulfate.

### (3) Electrical Potentials

H. Flood and T. Förland's[19] measurements of the breaking of oxygen bridges in pyrosulfate, borate and titanate systems reveal that in fused oxide systems acidity-basicity can be linked to the state of polarization of the $O^{2-}$ ions or, what is the same, to the polarizing action of the cations which surround and stabilize the $O^{2-}$ ion.

An oxygen atom can attract an electron and form an $O^-$ ion. This unit, however, has no tendency to complete its octet shell but will repel a second electron. The formation of an $O^{2-}$ ion is an endothermic process and requires the expenditure of nearly 200 Kcal. Nevertheless, it is permissible to treat silicates, borates, etc. as systems which contain $O^{2-}$ ions as building units because they also contain positive ions of sufficient field strength to stabilize the quantum state $O^{2-}$ and prevent its dissociation. In the extreme case in $Cs_2O$ where the $O^{2-}$ ion is neutralized by large and singly charged $Cs^+$ ions, the field is not sufficient to stabilize the $O^{2-}$ ions. $Cs_2O$ can be prepared at low temperature by the oxidation with air of metallic cesium dissolved in liquid anhydrous ammonia. This oxide, however, decomposes near 200°C into a peroxide and the metal.

The stability of the $O^{2-}$ ions in a fused salt or a glass can be measured by a galvanic cell and compared with the stability of $O^{2-}$ ions in other systems at the same temperature. We can picture platinum electrodes in air or oxygen inserted into a fused salt or glass as places where $O_2$ molecules change into $O^{2-}$ ions and $O^{2-}$ ions change into $O_2$ molecules. This dynamic equilibrium will be disturbed if the two electrodes are surrounded by melts of different compositions. In this case a potential difference is established between the electrodes and a current flows when the electrodes are connected. This current causes ions to migrate in the melt and one can assume that in glasses it is primarily the alkali ion which carries the current.

The dynamic equilibrium can also be disturbed by making the oxygen pressures at the two electrodes different. In spite of the simplicity of the system

$$(Pt)\ O_2\ :\ \text{Glass I}\ :\ \text{Glass II}\ :\ O_2\ (Pt)$$

the experimental difficulties are so great that little exact information on galvanic cells of this type is available. The classical example for such a reversible oxygen electrode in which the $O_2$ pressure is different is the glass cell which F. Haber[20] described fifty years ago.

P. Csaki and A. Dietzel[21] used electrical potential measurements for determining the "internal oxygen pressure" in a glass which contained an element such as iron in different states of oxidation. The internal oxygen pressure of a glass not only determines the light absorption of colored glasses but also is pertinent to the melting and fining operation. Just as one can use the color of chromic-chromate glass as an indicator for either its internal oxygen pressure or the basicity of the glass, so also can one use electrical potentials for both purposes.

Indeed, experiments carried out along these lines by M. Tashiro, T. Förland, G. S. Smith and G. E. Rindone[22] indicate that an alkali silicate can be made more acidic by replacing some of its $Na_2O$ by $SiO_2$, MgO or BaO. The values of the potentials reveal that MgO is a stronger acid than BaO but both oxides are more acidic than $SiO_2$.

### (4) Atomistic Interpretation of the Acidity of Glasses

Three independent experimental approaches, namely, the chemical resistivity of glasses, the color indicators, and the electrical potentials between different glasses using silver electrodes, led to the same result: CaO and similar oxides which are normally considered to be basic are strong acids when introduced into alkali borates or into alkali silicates. Their acidity is even greater than that of the acid constituents of these melts, i.e., of boric acid and silica respectively.

In order to give an atomistic explanation for this observation we have to choose the anionic approach to acidity (Section II, 2) because the only common constituent of these glasses is the $O^{2-}$ ion. We treat a system which contains $O^{2-}$ ions of low polarizability as an acid and a corresponding system which contains more polarizable $O^{2-}$ ions as basic with respect to the former. This definition permits us to rephrase our question "Why does CaO added to a sodium silicate glass behave as a stronger acid than $SiO_2$?" to the following: "Why do $Ca^{2+}$ ions have a stronger tightening effect upon the $O^{2-}$ ions of a sodium silicate than additional $Si^{4+}$ ions?" This question can now be answered. A sodium silicate glass contains essentially two types of $O^{2-}$ ions, one which is common to two $SiO_4$ tetrahedra often referred to as "bridging $O^{2-}$ ion" and another which belongs to only one $SiO_4$ group and which is neutralized by an alkali ion. These "non-bridging $O^{2-}$ ions" have the greater polarizability because they are polarized by only one $Si^{4+}$ and by the much weaker field of an alkali ion. Because of the weak field of the $Na^+$ ion we do not list as a separate species those $O^{2-}$ ions which are of the bridging type but which at the same time have an $Na^+$ ion as a neighbor. As a first approximation we may, therefore, assume that a change in the alkali-silica ratio affects only the ratio of briding to non-bridging $O^{2-}$ ions but not their respective polarizabilities. In other words, such a glass contains two types of anions, one of very low polarizability tightened by two adjacent $Si^{4+}$ ions and one of greater polarizability.

The addition of CaO to such a system introduces a new cation with a charge of two and a coordination of approximately six or more. In crystalline CaO the $Ca^{2+}$ ions are screened by six $O^{2-}$ ions (NaCl-structure) but it is possible that more anions are required if they are polarized by silicon ions. If $O^{2-}$ ions of sufficient polarizability are available, the CaO goes into solution by surrounding the $Ca^{2+}$ ions by six or more of these polarizable $O^{2-}$ ions. Pure $SiO_2$ or pure $B_2O_3$ cannot dissolve CaO because of the lack of polarizable $O^{2-}$ ions. This is the reason why the two systems CaO-$SiO_2$ and CaO-$B_2O_3$ have immisicibility gaps. A fused so-

dium silicate can dissolve CaO because it contains some polarizable $O^{2-}$ ions. In such a ternary glass the $Ca^{2+}$ ions will assume positions in which they are screened by six or more non-bridging $O^{2-}$ ions. This structure explains why CaO is so effective in increasing the acidity of the glass. Each $Ca^{2+}$ ion introduced into the melt as CaO brings in only one polarizable $O^{2-}$ ion but ties up at least six. Structurally speaking, the $O^{2-}$ ions of the $Si^{4+}$ $O^{2-}$ $Na^{+}$ groups are changed into $O^{2-}$ ions which are tightened by a $Ca^{2+}$ ion in addition to the $Si^{4+}$ and $Na^{+}$ ions.

## V. ON THE ACIDITY OF SOLIDS

We have seen in the preceding chapters that several methods are available for measuring the acidity-basicity of fused oxide systems such as salts, slags or glasses. For this purpose we derive the field strengths, the screening demands and the polarizing actions of cations from the tightening effect which they exert upon the anions.

The structural interpretation of the acidity of alkali silicate glasses revealed that the terms "acidity" and "basicity" cannot be applied to glasses in the same broad sense as they are used in connection with aqueous systems. An alkali silicate glass contains structural units which differ in their acidity. The absence of protons, i.e., of cations which can freely move without major activation energy, makes it impossible for these systems to equalize the degree of screening of all structural groups.

By retaining the concept of acidity for glasses and crystalline solids we should be aware of the fact that it has lost its original meaning and that it can no longer be used to describe the character of the system as a whole. This limitation has to be properly understood because we encounter this feature in many technically important processes. The chemical reaction of glasses with water has been discussed earlier. The interaction of clay minerals with water is of paramount importance for the fields of ceramics, paper chemistry, catalysis and secondary recovery of oil. Clay minerals can be acids. They can assume a negative charge when dispersed in water and they can react with basic compounds such as NaOH, $Ba(OH)_2$, etc. Their acidity is vested in cations which are incompletely screened and we must expect that this "acidity" of clay minerals is a function not only of the composition and the structure of the mineral but also of its particle size. The acidity of these particles should be greater for corners and edges than for the faces of the crystals.

When the basic constituents of a natural clay mineral have been removed and the "clay acid" is calcined, metastructures are formed which can have a very high acidity. These materials and their synthetic counterparts, the alumina-silica catalysts, behave like strong acids and they can send protons into organic molecules at elevated temperature so that they act as cracking catalysts. Because of the technical importance of these catalysts the literature on their structures and the source of their acidity is voluminous.

Another important group of reactions which involves acidity-basicity relations of solids is the hydration of calcium silicates and aluminates, a process which is responsible for the setting of hydraulic cements.

Our atomistic interpretation of the acidity of sodium silicate glasses must lead to the conclusion that introducing an indicator into the glass and moving it through the solid would reveal that the acidity changes from one spot to the next.

The proton and its rate of penetration into a solid can be looked upon as a tiny device, a probe, which allows one to examine the basicity of glasses at room temperature. When water is brought onto the surface of a glass, protons can enter the glass and as these protons diffuse into the interior they can be followed by $OH^{-}$ ions which restore electroneutrality. Quartz and cristobalite are stable in contact with water, a fact which indicates that for pure $SiO_2$ the equilibrium lies on the side anhydrous silica plus water. Complex silicate glasses contain $O^{2-}$ ions which are exposed to only one $Si^{4+}$ ion and weaker cations, e.g., $Na^{+}$ ions. The lower charge of the $Na^{+}$ ion and the asymmetry of the environment work in the same direction, they loosen the electron clouds of the $O^{2-}$ ions. In our terminology it would mean that the sodium silicate glass contains anions which are more acidic than water at room temperature and others which are more "basic" than water.

The question arises whether or not it is useful to speak of an "average acidity" or should one abandon this concept completely when referring to the solid glass. As we look upon this concept of acidity-basicity merely from the viewpoint of practicality and usefulness, we have to find out whether or not it will help us to understand the behavior of glass at ordinary temperature.

The fluctuation of the acidity can reach macroscopic dimensions. In this case a part of a glass can be leached out and the more acidic part remains. This is done in the Vycor-Process where a more basic sodium borate is dissolved by diluted acids and the more acidic skeleton remains.

A similar experiment has been performed in nature over geological times: the transition of obsidian into perlite. Obsidian is a natural silicate glass, a magma which has failed to crystallize on cooling. Over geological periods some obsidians have been partly or totally hydrated and thus formed the perlite. Whereas obsidian contains only little water (less than 1.0 per cent) perlite can contain up to 10 per cent water. Recently, C. S. Ross and R. S. Smith[23] examined such a rock consisting of perlite and inclusions of obsidian and obtained very interesting results which help us to better understand the interaction between glasses and water at ordinary temperature. They came to the conclusion that water must participate in these minerals in two ways. The water can be driven out of perlite at relatively low temperature, e.g., 500°C and lower, depending on the time, but the dehydration of obsidian requires temperatures of above 1000°C. This can be easily understood from the participation of the two types of "water" in the structures of obsidian and perlite. In no case can we expect $H_2O$ molecules to be present, but both structures contain $OH^{-}$ ions. The water in the obsidian consists of $OH^{-}$ ions which are more or less randomly distributed in the silicate where they take the places of occasional $O^{2-}$ ions. In order to escape as $H_2O$ molecules, the obsidian has to be heated to a high temperature in order to give the anions

(*Continued on page* 336)

# Inventions and Inventors

## Annealing and Tempering

*Glass Lehr. Fig. 1. Patent No. 2,711,616.* Filed January 19, 1952. Issued June 28, 1955. Nine sheets of drawings. Assigned to Surface Combustion Corporation by Harvey C. Weller and Clarke C. Sykes.

The present invention is directed to an improved lehr and conveyor system for annealing of glass ware with marked reduction in floor space and many benefits in economy of operation and quality of product. Ware is loaded on the trays in a loading position at the charge end, by a continuous belt-type stacker, indicated at belt 30 in Fig. 1. At the front or charge end of the lehr, the ware is picked up by rollers 32, on elevator chains 34, and carried upwards in the elevator 33, to the top of the lehr. A top, or first, past pusher 37, is utilized to unload the elevator and by pushing at one end of a row of trays at the top of the lehr, the last tray of that pass is loaded onto rollers, carried by a first lowering-elevator 38, at the rear of the lehr. The first lowering-elevator is lowered, with a tray on its upper support rollers, to a second position shown by dashed lines in Fig. 1, its upper support rollers are aligned with rows of rollers on the lehr forming a conveyor for the trays in a second pass of the lehr. This second pass terminates on a second, or middle, lowering-elevator 41. The deposited tray is then lowered to a third pass of the lehr by dropping the second lowering elevator to the position shown in full lines, from which a third pass pusher 43 moves the third pass of trays on its conveyor rollers 32, after which the ware is ultimately unloaded at the discharge end 23. With a closed-top furnace and an elevator shaft which is utilized to heat the ware or to equalize the temperature, at the desired annealing temperature, there is no loss of heating gas due to convection by the furnace stack action. With the various devices disclosed it is a relatively simple matter to vary the ware temperature properly as it passes downward through the body of the lehr in its cooling cycle. Since it is easier to vary and control cooling rates and temperatures from pass to pass than it is along a given horizontal pass, due to the inherent stratification of gases in a vertical chamber and the drift of gases always present in horizontal chambers, the vertical-type lehr is well adapted to design around a given annealing cycle.

The patent contains fifteen claims and the following references were cited: 270,929, Brockunier et al., Jan. 23, 1883; 1,152,969, Quimby, Sept. 7, 1915; 2,129,057, Greene, Sept. 6, 1938; 2,133,783, Merrill, Oct. 18, 1938; 2,370,381, Vaughan, Feb. 27, 1945, and 13,907, Great Britain, June 15, 1907.

## Furnaces

*Batch Preparing Device. Fig. 2. Patent No. 2,712,203.* Filed May 25, 1951. Issued July 5, 1955. Seven sheets of drawings. Assigned to Armstrong Cork Company by Clarence C. Green.

A device for preparing a series of individual batches of raw materials is shown in Fig. 2, in which the consecutive batches are not necessarily of the same forma-

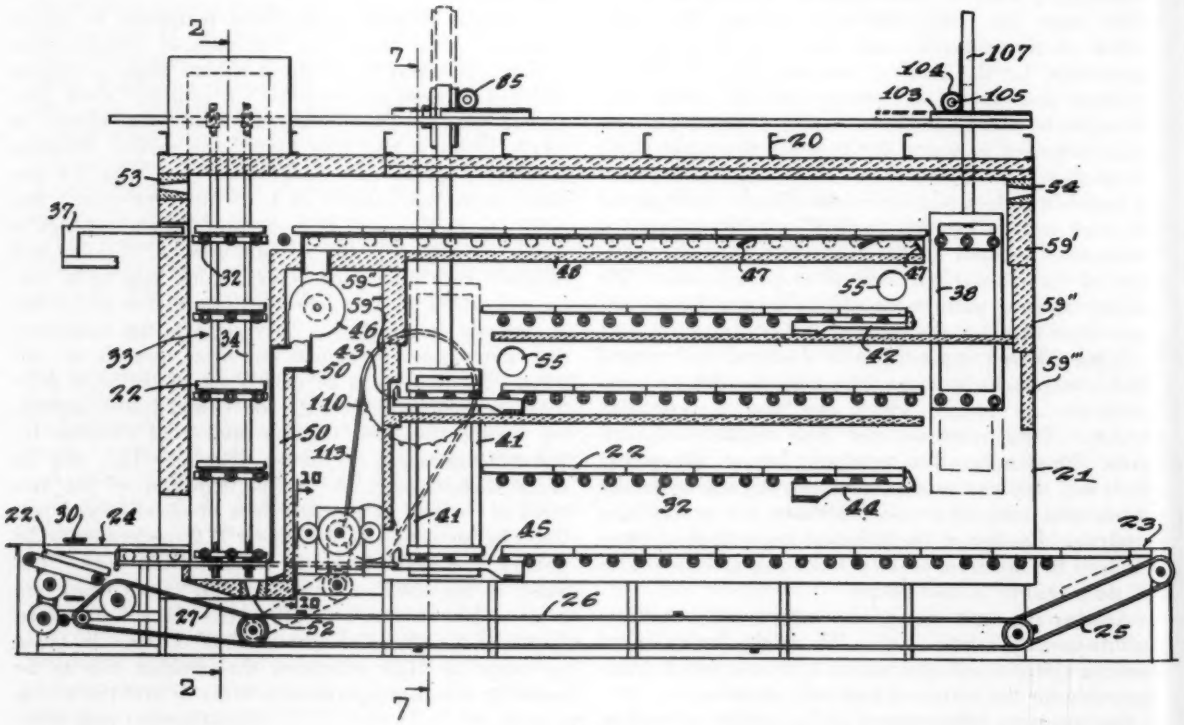


Fig. 1

tion. The device measures the proper amount of ingredients for a given formulation and delivers the measured batch to the proper storage tube. The system contains thirteen scales, having three beams each, to select raw materials to be placed in five storage tubes. Control is accomplished by means of a rotatable turntable, a plurarity of tiltable buckets containing the essential ingredents, which distinguish one batch from another, and manually set cams to control the movement of the buckets. It is possible to accurately control the quantity of each ingredients entering into a prepared batch of raw material and to insure that the proper proportion of raw materials will be present in all batches, and that the batches will keep their homogeneous nature as nearly as possible until they are delivered to the melting furnace. It is also possible to accurately control a plurality of batches, in process at one time, and keep them properly segregated from one another, so that there is no danger of two batches intermingling at any point on the equipment.

The patent contains four claims and the following references were cited: 1,867,489, Bennett et al., July 12, 1932, and 2,105,266, Rendall, Jan. 11, 1938.

### Glass Compositions

*Optical Flint Glass. Patent No. 2,723,203.* Filed October 1, 1952. Issued November 8, 1955. No drawings. Assigned to Ernst Leitz, G. m. b. H. by Weissenberg, H. Bredow, and N. Meinert.

The present invention relates to optitcal flint glasses of high refractive indices and good values of dispersion (the Abbe number V). These glasses are distinctive in that they are colorless and not attacked by the atmosphere. In the following tables examples are given of the compositions of the glasses.

TABLE I
(In percent by weight)

| Melt No. | $Pb_3(PO_4)_2$ | $Ca(PO_3)_2$ | $Na_3AlF_6$ | $n_D$ | V |
|---|---|---|---|---|---|
| M279 | 94.3 | 4.7 | 1 | 1.797 | 31.2 |
| M280 | 90.1 | 9.0 | 0.9 | 1.773 | 32.6 |

TABLE II
(In percent by weight)

| Melt No. | $Pb_3(PO_4)_2$ | $Ca(PO_3)_2$ | $InPO_6$ | $n_D$ | V |
|---|---|---|---|---|---|
| E286 | 87.0 | 8.7 | 4.3 | 1.766 | 33.6 |
| E287 | 83.4 | 8.3 | 8.3 | 1.7725 | 28.4 |
| E288 | 77.0 | 7.7 | 15.3 | 1.757 | 33.9 |
| E289 | 71.5 | 7.2 | 21.3 | 1.749 | 35.0 |
| E290 | 62.4 | 6.3 | 31.3 | 1.756 | 34.2 |
| E291 | 54.1 | 5.4 | 40.5 | 1.752 | 34.8 |
| E292 | 47.6 | 4.8 | 47.6 | 1.696 | 41.6 |

It is proposed that the lead orthophosphate be formed wet, as, for example, by a reaction of lead chloride with ammonium phosphate and the resulting lead orthophosphate be used as a charging material for the glasses of

(*Continued on page* 352)

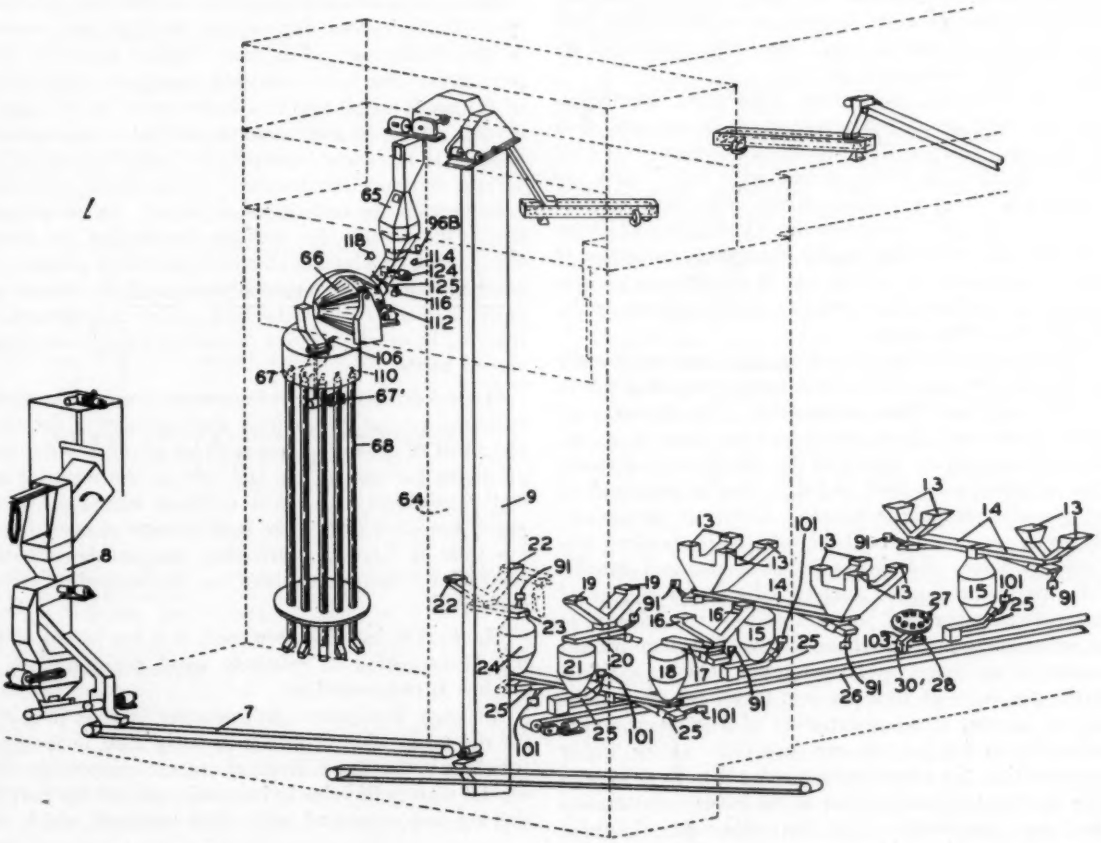


Fig. 2

## Rapid Methods of Analysis of Glasses and Glassmaking Materials

Chemical analysis has always been a useful investigational tool, but its main drawback in the silicate and glass fields has been the fact that the classical methods are quite time consuming. Over the past ten years, however, a good deal of time and effort has been spent, not so much in a search of increased accuracy, but in an effort to reduce the time required for these analyses. F. Hartley reviews the results obtained as a result of this search in the Vol. II, *Proceedings of the International Commission on Glass.* In general, the review deals only with those constituents which are of importance in normal glass making practice and only quantitative methods are included. The following summary, gives only the highlights of this review. The original paper should be consulted for the detailed list of references.

The application of spectrochemical methods to the analysis of inorganic materials is not new but only in recent years have they been improved so that analyses of sufficient accuracy have become possible. Laboratories in the larger glass works regard a spectrograph as an indispensable tool for the quantitative analysis of many of the materials normally encountered. The main attractions of these methods are the great economy in time, the satisfactory analysis of elements which involve difficult chemical separations and their high degree of accuracy at low concentrations.

It is in "emission" rather than "absorption" spectrography that most progress has been made in the strict field of analysis. The term "emission spectrography" is used here to include all forms of excitation from which the radiation is resolved and measured. The term "absorption spectrography" comprises those techniques which involve an analysis of the energy absorption properties of the material under examination. The latter may include measurements through a medium such as glass, or the investigation of powders.

The subject of emission spectrography can conveniently be discussed in separate sections dealing respectively with spectrography and flame photometry. The former comprises those methods in which the spectrum of a substance is excited by means of the electric arc or spark. The radiation is resolved and it is usually measured by using a photographic technique. For flame photometry the sample is dissolved and the solution is atomized into a suitable flame. Selected radiation is measured directly.

In the spectrographic analysis of silicates and allied materials an error of 2 per cent or less is considered to be satistfactory by present standards. Thus, an element present to the extent of 10 per cent could be analyzed within the limits of 10.2 per cent to 9.8 per cent, while for one present at a concentration of 5 per cent results within 5.1 to 4.9 per cent are expected. At the higher concentration, the tolerances are wider than those obtainable by chemical analysis, but at the lower concentration they are comparable. As the concentrate becomes lower, the precision of spectrographic analysis starts exceeding that of chemical methods.

The more usual constituents of glass which have been analyzed satisfactorily when present in a concentration of not more than 5 per cent include CaO, MgO, $Na_2O$, $K_2O$, BaO, $Fe_2O_3$, $Al_2O_3$, ZnO, $TiO_2$, $Sb_2O_3$, $MnO_2$, $Li_2O$, $B_2O_3$, and $Cr_2O_3$. Improvements in techniques are further reducing the error on constituents, such as the above, but it is unlikely that the direct determination of $SiO_2$ will be possible with a precision comparable with that of chemical methods. (*Editors note:* In most routine work, using chemical methods, $SiO_2$ is satisfactorily determined by difference. Spectrographic methods for sand also determine the impurities with great accuracy and the $SiO_2$ value is found by difference).

In the past, the determination of alkalies in glass and glass making materials was a tedious and slow process. The introduction some fifteen years ago of the triple acetate method for the analysis of $Na_2O$ removed this disadvantage, and a chemical analysis could be completed in about 5 hours. If, however, potassium had to be determined, this period was extended considerably and if lithium were present, a difficult separation was involved. In these circumstantces, a spectrochemical method offered advantages in speed and simplicity.

Flame methods are limited to those elements, the excitation of which does not require the high temperatures of the electric arc. For glass making materials flame photometry has been restricted mainly to the analysis of the alkali metals and to a lesser extent of the alkaline earths. A rapid and accurate method of analysis for alkalies is necessary primarily in order to control and correct the glass composition. Considerable differences exist between the techniques employed. In the preparation of the solution, for example, one method uses hydrofluoric acid, which takes about 15 minutes to prepare. In other methods the solution is evaporated to dryness and redissolved after which the $B_2O_3$ group and calcium are removed by precipitation, a procedure which must occupy several hours.

Marked differences have been noted between the claims made concerning the accuracy and precision of determining alkali in glasses. Some workers accept a wide range of results for one sample and rely on the mean of several determinations to yield sufficient accuracy. It appears, however, that if the approximate composition of the glass is known, a precision comparable with that achieved by chemical analysis can be obtained by certain methods.

The method has also been used, in a few instances, for the determination of relatively small concentrations of alkalies in raw materials.

Although absorption spectrography is used primarily for the study of structure, it is being used increasingly with success for the analysis of organic compounds. For several reasons its value in inorganic analysis has been restricted and compared with other methods which can

(*Continued on page* 360)

# Current Statistical Position of Glass

**Employment and payrolls:** Employment in the glass industry during March, 1956 was as follows: *Flat Glass:* A preliminary figure of 29,200 for March, 1956 indicates a decrease of 0.3 per cent from the adjusted final February, 1956 figure of 29,300. *Glass and Glassware, Pressed and Blown:* An increase of 0.7 per cent is shown by the preliminary March 1956 figure of 79,700 compared with the final February 79,100 figure. *Glass Products Made of Purchased Glass:* The preliminary March, 1956 figure of 15,600 indicates a decrease of 0.6 per cent from the previous month's adjusted figure of 15,700. Payrolls in the glass industry during March, 1956 were as follows: *Flat Glass:* A decrease of 3.5 per cent is shown in the preliminary $13,783,276 when compared with February's adjusted $14,281,113. *Glass and Glassware, Pressed and Blown:* An increase of 4.1 per cent is shown in the preliminary $27,345,867 reported for March, 1956 when compared with the previous month's adjusted $26,259,618. *Glass Products Made of Purchased Glass:* A preliminary figure of $4,567,680 was reported for March, 1956. This is 2 per cent lower than the adjusted February figure of $4,658,975.

**GLASS CONTAINER SHIPMENTS**
(All Figures in Gross)

**Narrow Neck Containers**

| | April, 1956 |
|---|---|
| Foods | 1,019,000 |
| Medicinal and Health Supplies | 1,284,000 |
| Chemical, Household and Industrial | 793,000 |
| Toiletries and Cosmetics | 709,000 |
| Beverage, Returnable | 714,000 |
| Beverage, Non-returnable | 94,000 |
| Beer, Returnable | 340,000 |
| Beer, Non-returnable | 644,000 |
| Liquor | 853,000 |
| Wine | 369,000 |
| Sub-total (Narrow) | 6,819,000 |

**Wide Mouth Containers**

| | |
|---|---|
| Food | *2,679,000 |
| Medicinal and Health Supplies | 406,000 |
| Chemical, Household and Industrial | 170,000 |
| Toiletries and Cosmetics | 209,000 |
| Packers' Tumblers | 119,000 |
| Dairy Products | 188,000 |
| Sub-total (Wide) | 3,771,000 |
| Total Domestic | 10,590,000 |
| Export Shipments | 249,000 |
| TOTAL SHIPMENTS | 10,839,000 |

* This figure includes Fruit Jars and Jelly Glasses.

**GLASS CONTAINER PRODUCTION AND INVENTORY**
(All Figures in Gross)

| | | Production April, 1956 | Stocks April, 1956 |
|---|---|---|---|
| Foods: Medicinal and Health Supplies; Chemicals, Household and Industrial: Toiletries and Cosmetics | Narrow Neck ... | 4,263,000 | 5,160,000 |
| | Wide Mouth .. | *3,849,000 | *5,261,000 |
| Beverage, Returnable | | 976,000 | 1,449,000 |
| Beverage, Non-returnable | | 127,000 | 206,000 |
| Beer, Returnable | | 415,000 | 481,000 |
| Beer, Non-returnable | | 712,000 | 908,000 |
| Liquor | | 904,000 | 1,034,000 |
| Wine | | 398,000 | 501,000 |
| Packers' Tumblers | | 127,000 | 171,000 |
| Dairy Products | | 214,000 | 378,000 |
| TOTAL | | 11,985,000 | 15,549,000 |

* This figure includes Fruit Jars and Jelly Glasses.

**Glass container production** based on figures released by the Bureau of Census for the month of April, 1956 shows a rise to reach 11,985,000 gross. This is an increase of 1 per cent over March, 1956 production of 11,865,000 gross. Production in April, 1955 was 11,045,000 gross, which is 7.8 per cent below this year's April production. Thus far in 1956, glass container production reached 36,077,000 gross. In a similar period last year the production was 42,882,000 gross which was 16 per cent over this year's production.

Shipments of glass containers during April, 1956 fell off to 10,839,000 gross. This is an 11 per cent decrease of the previous month's 12,170,000 gross and an increase of 1.3 per cent over April, 1955 shipments, which were 10,696,000 gross. Preliminary total shipments for the first four months of 1956 rose to 42,995,000 gross, which is 5.3 per cent higher than the corresponding period last year.

Stocks on hand at the end of April, 1956 were 15,549,000 gross. This is 7.1 per cent higher than the 14,516,000 gross at hand at the end of the previous month or the 14,521,000 gross at hand at the end of April 1955.

**Automatic tumbler production** during March 1956 was 5,136,293 dozens. This is a decrease of 10.3 per cent from last year's March production of 5,724,878 dozens. Production this year so far has been 15,785,050 dozens. Shipments during March 1956 rose to 5,114,034 dozens, an increase of 10 per cent over February 1956, 4,641,469 dozens. Shipments in March 1955 were 5,619,096 dozens which is 9 per cent higher than March 1956 shipments. During the year 1956, shipments reached 14,241,269 dozens or 6.5 per cent lower than 1955's first three months 15,237,242 dozens. At the end of the 12 month period ending March 31, 1956, shipments were 61,543,911 dozens, or 1.9 per cent lower than the shipments in the twelve month period ending March 31, 1955.

**Table, kitchen and household glassware:** Manufacturers' sales of machine-made table, kitchen and household glassware during March 1956 rose to reach 3,529,834 dozens. This is an increase of 10.3 per cent from the February 1956 figure of 3,188,000 dozens, and 3.9 per cent lower than March 1955 3,672,086 dozens. At the close of the twelve month period ending March 31, 1956 manufacturers' sales were 37,096,799 dozens, 1.8 below the 37,759,516 dozens sold in a twelve month period ending March 31, 1955.

## Acid Base Relationship . . .

(*Continued from page* 331)

the mobility which is necessary for two $OH^-$ ions to meet and to react, according to

$$OH^- + OH^- = O^{2-} + H_2O.$$

In perlite we have the same situation as in the obsidian from which it has formed, but in addition we have $OH^-$ ions which exist in pairs. In order to maintain electroneutrality in the smallest possible volume, the formation of perlite from obsidian

$$O^{2-} + H_2O \longrightarrow 2\ OH^-$$

consists of the penetration of the proton of water into one of the more polarizable $O^{2-}$ ions of the obsidian and the addition of one $OH^-$ ion to the neighboring cation. For this reason the "perlite water" occurs in $OH^-$ pairs and can escape as $H_2O$ molecules at a much lower temperature than the "obsidian water" which consists of widely scattered single $OH^-$ ions.

In crystals the screening demand or the energy gained by additional screeners may vary considerably from one cation to another. Color indicators reveal that water or aqueous solutions can have surfaces which differ in acidity from the bulk. As far as the surfaces of crystals are concerned, we may evaluate the potential difference between solids and water in terms of acidity. Finely powdered quartz suspended in pure water assumes a negative charge but iron oxide assumes a positive charge. This would mean that silica is acidic and iron oxide basic with respect to neutral water.

The anionic approach, i.e., the use of the polarizability of the anions as a measure of acidity, allows us to refer to BaO as a base with respect to $SiO_2$ as an acid. However, the question still remains: How useful is this concept in solid state chemistry? One might answer by stating that this description of CaO as a base and $SiO_2$ as an acid makes it possible to consider the reaction between the two solids as one of salt formation. A mixture of $SiO_2$ and CaO can lower its free energy by reacting in a fashion which surrounds the $Si^{4+}$ ion by $O^{2-}$ ions which are more polarizable than those of $SiO_2$. Thus, we can explain why $SiO_2$ and CaO form compounds such as $CaSiO_3$ and $Ca_2SiO_4$. However, the reactivity of $SiO_2$ with CaO does not stop when the orthosilicate ratio is reached, i.e., a ratio in which each silicon has a chance to form isolated $SiO_4$ tetrahedra. This raises the question: Why does the compound $3\ CaO \cdot SiO_2$ form? No doubt we must have reached the limit of usefulness of the acid-base concept. There must be other factors besides salt formation or improving the screening of the strongest cation which have to be considered.

Tricalcium silicate exists as a stable phase only in a limited temperature range and it is not stable at room temperature or at 2000°C. The orthosilicate of calcium forms several modifications. As far as the structure of these silicates is known it seems that the high temperature form of $2\ CaO \cdot SiO_2$ as well as the $3\ CaO \cdot SiO_2$ contains $Ca^{2+}$ ions in a very asymmetrical environment. It is unknown for crystals which are stable at ordinary temperature that a cation of the noble gas-type occurs in a strongly asymmetrical coordination. W. Buessem and A. Eitel[24] determined the structure of a calcium aluminate of the formula $12\ CaO \cdot 7\ Al_2O_3$ and found that the $Ca^{2+}$ ions are screened by four $O^{2-}$ ions but that the latter are all located on one side of the $Ca^{2+}$ ion. On the other side of the $Ca^{2+}$ no $O^{2-}$ ions were found in close proximity. They describe this unusual structure as an oxygen "basket" containing a $Ca^{2+}$ ion. This basket structure seems to be characteristic for the high temperature form of $2\ CaO \cdot SiO_2$ as well as for $3\ CaO \cdot SiO_2$. According to J. W. Jeffrey[25], tricalcium silicate is built from discrete $SiO_4$ tetrahedra and separate $Ca^{2+}$ and $O^{2-}$ ions. Again the $Ca^{2+}$ ions are surrounded by $O^{2-}$ ions in an asymmetrical fashion. Five $O^{2-}$ ions form a kind of basket around the $Ca^{2+}$ ion but only one $O^{2-}$ ion screens the other side of the $Ca^{2+}$ ion.

These asymmetrical units which seem to be characteristic for three constituents of the portland cement clinker, i.e., $3\ CaO \cdot SiO_2$, $2\ CaO \cdot SiO_2$ and $12\ CaO \cdot 7\ Al_2O_3$, make it possible for these compounds to react with water fairly rapidly. Their formation must be the result of the gain in entropy through stronger $Ca^{2+}$ vibrations. The $Ca^{2+}$ ions seem to be more flexible with respect to their coordination requirements than $Si^{4+}$ ions. The formation of "asymmetrical units" make possible high vibrational energies, thus stabilizing these odd crystal structures at high temperatures. At ordinary temperature the two silicates are metastable and react with water in order to complete the coordination of the $Ca^{2+}$ ions. This leads us to the conclusion that the compound $3\ CaO \cdot SiO_2$ owes its existence to the gain of entropy and not of potential energy. We cannot link the reactivity of these cement minerals, in particular their hydraulic properties, to their acidity or to their chemical composition. We cannot even link the reactivity of the $2\ CaO \cdot SiO_2$ to its lattice as a whole because the reactive, high temperature form is much more dense than the unreactive low temperature form. We have to distinguish between certain incompletely screened $Ca^{2+}$ ions and normally screened $Si^{4+}$ ions so that the application of the term "acidity" to a compound or to a lattice structure as a whole has lost its meaning.

In the field of silicate chemistry we find another group of compounds or systems which has lost screening and has become more "acidic" through gain of entropy: the metakaolin and related structures. The mineral kaolin has the empirical formula $Al_2O_3 \cdot 2\ SiO_2 \cdot 2\ H_2O$ and its water of constitution participates in the lattice as $OH^-$ ions. The $OH^-$ ions are typical for this group of clay minerals in which they screen $Mg^{2+}$ or $Al^{3+}$ ions. At approximately 400° - 500°C these minerals become unstable and the system gains entropy by releasing $H_2O$ molecules. This temperature, however, is too low for the residual constituents to arrange into a new equilibrium structure. It seems that the $Al^{3+}$ ions are the ones which lose most screening when kaolin changes into metakaolin. According to L. Tscheischwili, W. Buessem and W. Weyl[26], the $Al^{3+}$ ions in metakaolin are surrounded by four $O^{2-}$ ions but the structure does not permit these ions to assume the equilibrium distance which would allow proper screening of the $Al^{3+}$ ions. Metakaolin is very reactive, e.g., it can be used as an acid cracking catalyst. Its extreme "acidity" can also

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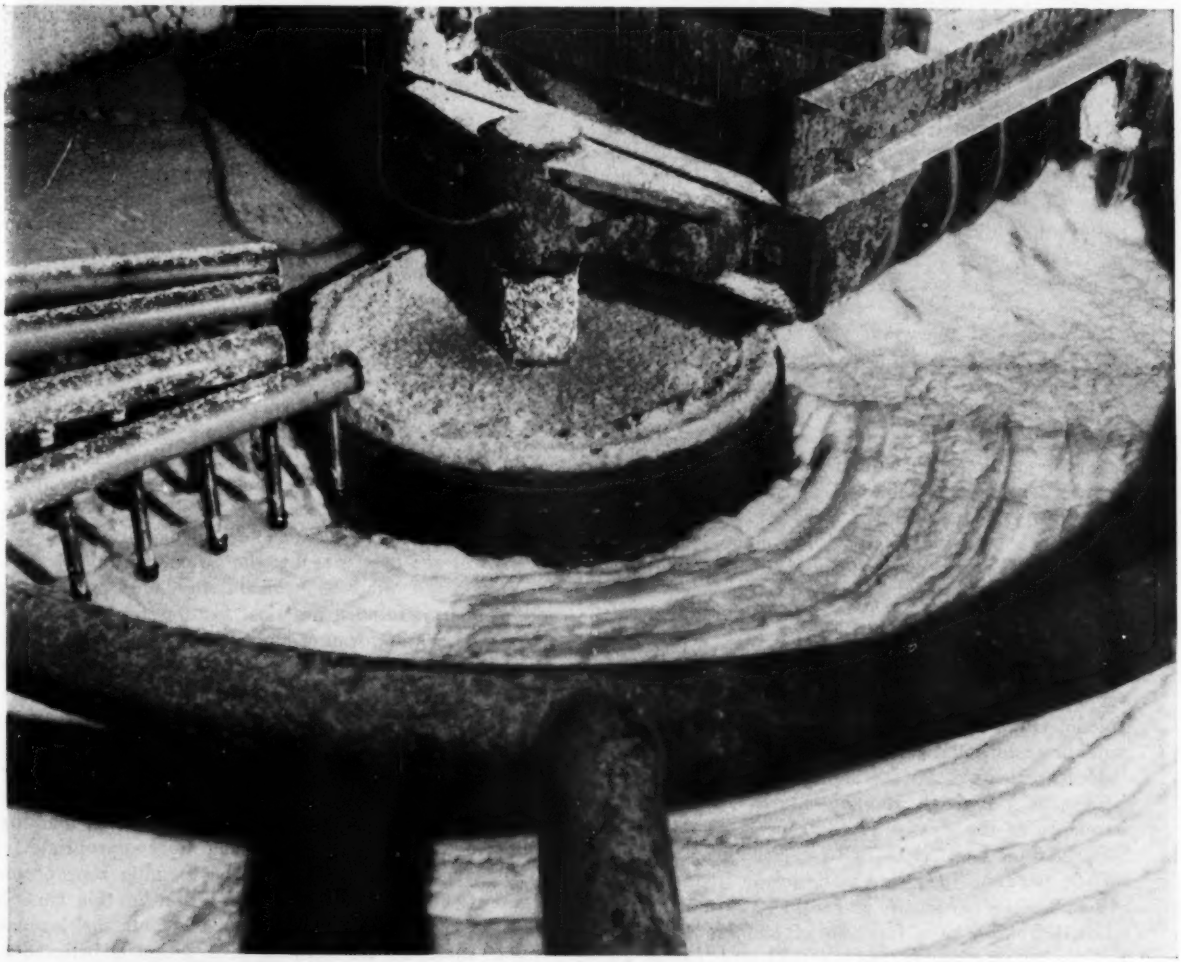

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## Glass Division at A.C.S. Meeting . . .

(*Continued from page* 320)

gated. Calcium was shown to improve the durability of potash-silica glasses much more than it does that of the soda-silica glasses. When calcium oxide replaced silica by 5 per cent, the potassium ion became more tenaciously held than the sodium. Calcium also lowered the maximum in the curve, ultimately changing it to a minimum.

The next paper, "Measurements of Dielectric Loss of Glass at Low Frequencies", by H. T. Smyth, and W. C. Lo, School of Ceramics, Rutgers University, New Brunswick, New Jersey was presented by Mr. Lo. Knowledge of dielectric loss at low temperatures is important to the theoretical concept of the structure of glass. The relation of the dielectric loss, generally represented by tan $\delta$ with temperature and frequency, has often been studied as a tool in research into the structure of glass. A method was described for measuring tan $\delta$ as a function of temperature at frequencies in the order of 1 cycle per second. Details of the electric circuit and the method of testing were given. Data on window glass were set forth, and the practical aspects, as well as the theoretical, were evaluated.

The next paper, "Modulus as a Function of Temperature and Thermal History by a Vibrating Reed Method", was written and presented by Michael Yamin, Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania. A rather simple apparatus and method of measuring Young's modulus of glasses were described. The method utilizes the vibrating-reed technique in which a thick fiber or simple rod test specimen is fused to a silica rod. The technique permits the measurement of the modulus as a function of temperature up to 1100° C. Absolute values of modulus can be determined quickly to within 4 or 5 per cent, and values of modulus of the same sample at different temperatures can be compared within a few tenths of a percent. The technique was shown to be of value to annealing behavior of glass because the modulus is more sensitive than the density or refractive index to the "fictive" temperature of the glass. Data were presented on a borosilicate glass fiber composition, Pyrex, vitreous silica, and a meta-phosphate glass. High degrees of quenching can also be observed by means of the techniques described.

"Two Peaks in the Internal Friction as a Function of Temperature in Some Sodium Silicate Glasses", was written by K. E. Forry, Owens-Illinois Glass Company, Toledo, Ohio. Mr. Forry presented a theoretical paper providing additional data on some sodium silicate glasses.

Measurements of the mechanical loss factor or internal friction as a function of temperature, composition, and frequency of the glasses 17 per cent $Na_2O$–83 per cent, $SiO_2$, 25.6 per cent $Na_2O$–74.4 per cent $SiO_2$, 34 per cent $Na_2$–66 per cent $SiO_2$ were made in the frequency range of 1 to 3 cycles per second and from $\pm$90° to 500° F. The internal friction as a function of temperature revealed two distinct maxima for each glass tested, one of which occurred in the temperature range of –50° to 75° F., and the other in the range of 300° to 500° F. The low temperatures at which both peaks occurred increased with increasing frequency and decreased with increasing sodium content. Also, the height of the low temperature peak was practically linearly dependent upon the sodium content. Such was not the case for the high temperature maxima. The activation energies associated with each peak were calculated from the temperature shift with frequency change of the peaks to be 14 to 25 kcal. per mole for the low temperature peak and 21 to 34 kcal per mole for the high temperature peak depending on the sodium content. The period of oscillation was observed with each internal friction measurement and its variation with temperature used to calculate the dynamite shear modulus as a function of temperature.

The next paper, "Precision Glass, Fabrication and Uses," was written by Oscar H. Grauer and William Conway, Fischer and Porter Company, Hatboro, Pennsylvania and was presented by Mr. Grauer. The manufacture of precision glass for specific purposes was described, and its prominence in precision instrumentation was stressed. Glass tubing is the most important form. In its fabrication, reforming and preforming operations usually involve shrinkage over a heated mandrel. Devitrification and annealing problems assume great importance as dimensional tolerances of $\pm$ 0.001 to $\pm$ 0.0001 in. are often required. Precision-bored tubing in cylindrical, square and oblique cross sections were shown. The glasses varied from borosilicate, Vycor, fused silica, lime-glass to lead glass compositions. Defects such as striae, stones, bubbles, hair-lines, dog-hair, and air-lines were discussed and shown to be involved in the various manufacturing processes. The close dimensional tolerances permit precision to glass components of instruments ranging from simple capillary tubes to a battery of flowrator meters.

"Electron Tube Ceramic Requirements and Manufacturing Considerations", was written and presented by A. G. Reimann, Tube Department, General Electric Company, Schenectady, New York. This paper emphasized the importance of the ceramic components of modern electron tubes. No reference was made to the glass requirements. The ceramic components are composed principally of forsterite, zircon, cordierite as well as molybdenum, stainless steel, alumina and other alloys. The important properties are a good coefficient of expansion match and simple design which will provide the desired fit and proper seal to the assembled unit.

Methods of production, including body preparation, design considerations, practical features of die construction, methods of forming and control tests used were all discussed. The paper was an extremely informative one, related to glass components.

"Four-Functional Zones in Glass Tanks," was written by L. Penberthy and L. Miller, Penberthy Electromelt Company, Seattle 16, Washington. Mr. Penberthy proposed to divide the glass tank into four zones rather than the conventional three. He considered the melting, foaming, fining, and working zones as being more appropriate for the conventional glass tank. The foaming zone occurs right after the dog house, and action in this zone is highly important because it influences both melting and fining rates. In the foaming area action is believed to be largely solution rather than melting. Tests indicated that the surface of the glass in this area was quite high in silica, (80 per cent + $SiO_2$). Results of tests on heat-transfer and heat-reflection of foam indicate that these areas should be reduced or avoided. Generally speaking, these areas are reduced by electric boosting.

In a discussion of the paper, it was pointed out that a

(*Continued on page* 340)

Petrographic equipment provides service for glass customers in stone identifications and in the study of raw materials and finished products.

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# *Milestones* in Glass Progress

PHOTO COURTESY THE TOLEDO MUSEUM OF ART

*1810* Much of the social history of England was written in a word or a line on its drinking glasses. Many of the glasses bore inscriptions of political interest, as does the so-called Election Glass, above. Full inscription reads: "The Independence of Durham and Richd. Wharton its Defender."

*1890* Michigan Alkali Company, now a division of Wyandotte Chemicals Corporation (South Plant, above), was founded by Captain J. B. Ford to supply Soda Ash to the glass industry. Wyandotte has grown up with glass. Today, as in the past, it is a working partner, supplying technical assistance and raw-material chemicals to those great companies marking milestones in glass progress.

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## Glass Division at A.C.S. Meeting . . .

(*Continued from page* 338)

high-state of boiling is desirable in a tank for the production of good glass; however boiling and foaming are not believed to be synonymous.

The next paper, "The Contributions of Electric Melting and Boosting to Glass Technology", by P. LaBurthe and G. de Piolenc, Saint-Gobain, Inc., New York 36, New York, was presented by Mr. de Piolenc. For the past half century many patents have been issued in the field of electric melting in glass. Saint-Gobain, Paris, France, has been a great contributor and user of electric melting, and, therefore, the presentation of this paper created very much interest.

The electrical conductivity of glass is determined by its structure; only the metal ions contribute to its conductivity. The conductivity will, therefore, be a function of the concentration in metallic ions and of their mobility; the mobility in turn is a function of the molecular diameters and of the viscosity of the medium.

For practical purposes, it may be assumed that only the smallest ions, sodium and potassium, contribute to conductivity; this assumption is substantially true for glasses having over 12 per cent $Na_2O$.

The amount of heat required to melt the batch materials and cullet and take care of chemical reactions between constituents varies according to the composition and temperature at which the glass is used but it is in the vicinity of 270 WH/lb of molten glass using 30 per cent cullet.

For the sake of comparison only, a 270 sq. ft. area tank will produce, usually, 33 tons/day of glass of window glass quality with a maximum power of 2500 KW. The specific input is therefore 910 WH/lb and the average energy input rate in the tank is in the vicinity of 2.8 KW/cu. ft.

Four materials are currently in use and selected according to both their conductivity and heat resistance: iron, graphite, molybdenum, and platinum.

All the fully electric glass tanks in Europe are believed to be operating with graphite electrodes, but different results are obtained with different graphite qualities. Graphite electrodes have the following advantages: (1) They are light, and, in the event of breakage, float on the glass. (2) They are mechanically strong and more hot than cold. (3) They are very durable; in the hottest areas of the tank they have a life of 4 to 12 months, according to location. (4) They are moderate in cost and do not show up as an important item in the manufacturing cost. (5) They are suitable for tanks of all sizes.

Different types of electric tanks and electric boosting methods which have been used in Europe were shown. Some of the more interesting included several involving the use of molten tin as an electrode. Other electrodes constructed from porous graphite with a hollow core permit the escape of gases by hydrostatic pressure into the center of the core. This construction provides additional facilities for the gas contained within fine seeds to escape instead of slowly rising to the surface and then bursting.

When properly installed, electric melting improves the rate of melting on solid raw materials, increases the output of the furnace, reduces the wear on refractories, facilitates the removal of fine seeds, improves the homo-

geneity of the glass, where electricity is available at reasonable rates, reduces the temperature differential between top and bottom glass, cleans the tank of stratified materials, promotes improved temperature control, and improves the efficiency of flame heating.

These advantages have been achieved over a period of many years of intensive research and experimentation. The art of electric melting has become a science, and results can be assured, provided that the installations embody a number of exact principles.

"Study of the Surface Structure of Glass as Related to Its Durability", by Harold E. Simpson, the New York State College of Ceramics, Alfred University, Alfred, New York, was the next paper to be presented.

Cyclic humidity tests have been developed and described which have been useful in the evaluation of ground and polished plate glass, fire-polished window glass, optical reticules, ranging from optical crown glass to heavy flint glasses and various container and bottle glasses. The breakdown of these glasses was measured by means of a haze meter.

The question has been asked: what erosion products are present when glass surfaces fail, and what might be the mechanism of breakdown? With the hope of revealing the nature of these surface failures, electron microscope studies were made. These studies involved replication of the varying eroded surfaces, and it was found possible either to replicate replicas of eroded surfaces or to make replicas directly from the eroded surface.

Electron micrographs at high magnification (1900X to 5800X) have revealed the various etched patterns of the different glass surfaces. The eroded patterns were seen to vary considerably with different type glasses. The first products of weathering appeared to be carbonates of the alkalies and alkaline earths leaving a rather pronounced tracery or silica shell.

It would appear that a combination of controlled deterioration brought about by the use of the cyclic humidity tests, glass surfaces may be weathered to any desired stage, and by means of the electron replica technique an enlarged view of the destruction of the area surfaces may be seen.

It is hoped that by a combination of these techniques, a better knowledge of not only the durability but the chemistry of the surface of the glasses may be revealed.

The final paper of the Wednesday morning session was, "Thermal Expansivity of Binary Alkali Silicate and Alkaline Earth Borate Glasses", by H. F. Shermer, National Bureau of Standards, Washington 25, D. C. Thermal expansivity of binary alkali silicates and alkaline-earth borate glasses were measured interferometrically from room temperature through their deformation points. These results were correlated with liquid density data obtained on the same compositions. This research program was a part of a more extensive program sponsored by the National Bureau of Standards to contribute and to enhance knowledge of the structure of glass.

With lithium silicates, the expansion increased as lithium increased, while lithium borates showed a decrease in expansion with increase in lithium. Density measurements indicated an increase in density with lithium in lithium borates.

Potassium borates indicated a minimum value was reached as potassium was increased.

Calcium borates showed a slight decrease in expansion and decrease in density as calcium is increased. The paper provided considerable discussion concerning the likely role of boron in the various property trends.

The first paper of the Wednesday afternoon session was "The Inadequacy of the Fictive Temperature Concept", by H. N. Ritland, Corning Glass Works, Corning, New York. Data obtained on samples that were cooled or annealed at a definite "rate" and samples that were "soaked" or treated to equilibrium at different temperatures indicated that a single parameter is not sufficient to describe the effects of heat treatment. A number of physical properties, such as density, refractive index, thermal expansion, electrical conduction, light scattering, and rate of approach to equilibrium at constant temperature, were determined. Generally speaking, the "rate" samples showed less scattering of data than the "soaked" samples. Considered separately, samples annealed at various constant rates formed a homologous group, as do samples treated to equilibrium at different temperatures, but marked differences existed between the two groups. Nevertheless, the fictive temperature approximation in which the structural state of the glass is specified by a single parameter has proved very useful in the description of transformation range structural changes. The data were obtained on a borosilicate crown glass but the results are believed to be applicable to other glasses as well.

The second paper of the Wednesday afternoon session was, "Structural Interpretation of Low-Temperature Heat Capacities of Silica," by S. W. Barber and M. Dank, Owens-Illinois Glass Company, Toledo, Ohio. The paper was presented by Mr. Barber. Efforts to broaden and enhance the knowledge of the structure of glass by further measurements of physical properties have been made. Mr. Barber presented results from elasticity, spectra, and X-ray diffraction data which were correlated with new data in heat capacity between 5 and 300° K. It was proposed that a "unit cell" of about 4 $SiO_2$ exists and that more low frequency energy states exist in this material than are calculated from the elasticity and the known spectra. It was also found that $C_v$ at T 30° was analogous to that of lamillar structures and that $C_v$ vs. T for vitreous silica can be translated into that for BN by a simple change of temperature scale at T up to 300° K. It was suggested that the units be called "macrocules" and that they are many times larger than the unit cells of cristobalite. The internal structure is anistropic and nearly crystalline at the center. The paper provided considerable discussion in which a variety of opinions were expressed in regard to the proposed interpretations.

The next paper, "Interaction of Alkali and Alkaline-Earth-Ions in Simple Silica Glasses", was written by Rajeshwar K. Gupta and Robert L. Hess. Mr. Hess presented this third paper in a series devoted to durability of glass. In proposing a structure for glass, Hess believes that the positive ions of the so-called nonglass forming oxides exist in a preferential form rather than a random arrangement. He classifies the so-called hole positions into A, B, and C types based on the pairs and types of bridging oxygens. This classification provided a preferential grouping of secondary alkali ions that has a profound influence and provides an explanation of the many physical properties of glass.

Effect of the presence of additional alkali and alkaline-

earth ions in a glass on the diffusion rate of an alkali ion was discussed. The theoretical basis for the effect and its importance in determining the atomic structure of a glass were considered. The role of the individual ion diffusion rates in determining the total alkali extraction (which is also a measure of chemical durability) from a mixed alkali or alkali-alkaline earth silicate glasses was emphasized. The necessity of an exhaustive study of this interaction of the positive ions glass was pointed out.

The next paper, "Structural Interpretation of Immiscibility in Glass Systems Part I, Analysis and Calculation of Immiscibility," by Ernest M. Levin and Stanley Block, National Bureau of Standards, Washington 25, D. C., was presented by Mr. Block. The property of immiscibility in glass systems is one of great importance and of vital interest to all manufacturers of glass products. Immiscibility is often times the limiting factor that divides good and bad glasses. Immiscibility is also a governing factor in the formation of homogeneous glasses. Crystal chemistry principles were applied to the interpretation of immiscibility in known and unknown binary and termary systems. Starting with ionic radii and densities of end members (i.e. glasses and metal oxides), the authors calculated immiscibilities in binary borate and silicate systems. The results were of remarkable accuracy and shown to be within 4 to 5 per cent of the experimental values.

Immiscibility was most pronounced in borate glasses. A study was made in such systems involving CaO, MgO, ZnO, SrO, BaO, CdO, CoO. The immiscible areas were shown to be those high in $B_2O_3$ and or high in the modifying oxides.

The method was also expanded to include calculations of immiscibility in three component systems. The locus of limiting composition can be plotted and the areas of better glass formation shown. The paper provided considerable discussion, and the practical value of the data were apparent. It is hoped that techniques will be applied to other systems of specific interest to industry.

In the next paper of this group, "Structural Interpretation of Immiscibility in Glass Systems Part II: Coordination Principles Applied to Immiscibility", Stanley Block and Ernest M. Levin, National Bureau of Standards, Washington 25, D. C., Mr. Block expanded the concept of immiscibility in glass to explain structure.

The primary cause of immiscibility or tendency toward immiscibility, is the incompatibility of the coordination polyhedra of the network former and modifier ions. Electrostatic bond strength, defined as the valence divided by the coordination number, essentially determines the form of the liquidus curve, e.g., straight line, "S" shaped, or completely immiscible. The relation between electrostatic bond strength of the metal and the charge distribution on the silicon and/or boron tetrahedron governs the type of coordination assemblage that forms. A structure of glass is developed from the results of the application of the crystal chemistry principles.

The structure implications were discussed on the basis of (1) ionic nature of modifiers, (2) holes in the $SiO_2$ network, (3) two coordinating types given as A and B, (4) structural differences and (5) degree of order.

The paper was an attempt to correlate fundamental information and apply such information to practical use. It thus provided much discussion.

The last paper, "A Possible Explanation of Immiscibility in Silicate Melts", was written and presented by Mr. E. C. deWys, Owens-Corning Fiberglas Corporation, Newark, Ohio. Mr. deWys continued the theoretical approach of the explanation of immiscibility in silicate melts by first reviewing previous theories. It was pointed out that immiscibility is often a characteristic of certain cations like calcium, magnesium, and strontium. In addition, the $Si_2O_5$ structure is often present. Furthermore, the polarizing power of Si ions is far greater than other ions in glass. It is also believed that the two liquid phases involved in immiscibility may be divided by two mirror planes. This characteristic may be pronounced in borate systems that are likely to show immiscibility.

It appears that immiscibility in silicate melts is related to the presence of certain types of ionic structures in such liquids. It is felt that immiscibility might be explained in terms of deformative effects on such liquid structures. A search of the data on numerous chemical systems indicated that they correlate well with this theoretical approach.

A full business meeting was carried out under the chairmanship of August C. Siefert, Owens-Corning Fiberglas Corporation, who first gave a summary of the accomplishments of the past year. Progress is being made in the efforts to standardize glass testing with the use and development of so-called standard glasses. C. H. Hahner, National Bureau of Standards will be chairman of a Standard's Committee, with N. J. Kreidl, Bausch & Lomb Optical Company, as consultant.

The following reports were made: Program Committee —J. W. Michener, chairman, has found that Bedford Springs, Pennsylvania is a preferable location and that Thursday and Friday are the best meeting days. Technical papers with definite time limit are desirable.

Symposium Committees—S. D. Stookey, chairman. All symposia subjects formerly submitted have been covered. "Surface phenomena" have been suggested as a suitable subject for interest for future symposia. A new letter for suggestions should be sent out.

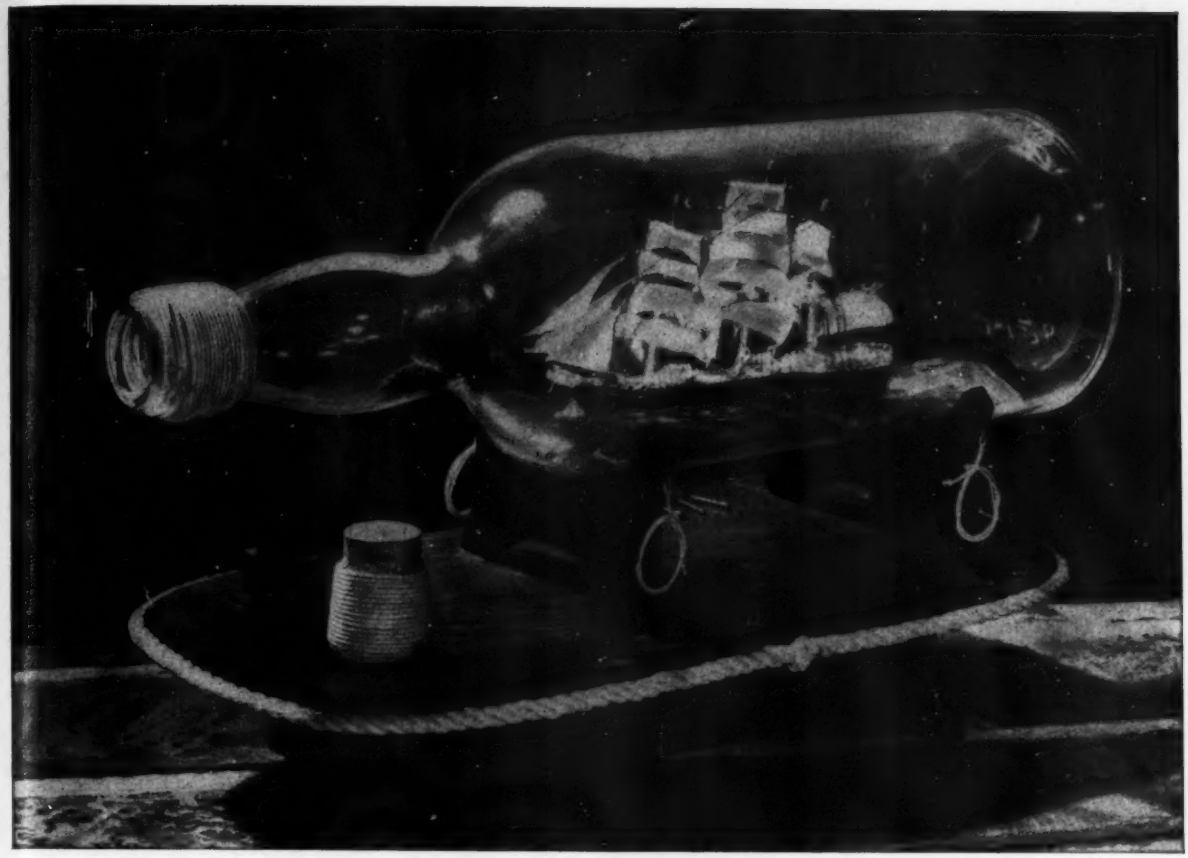
Research Committee—N. M. Brandt, chairman. Mr. Brandt stated that his committee will cooperate with other Research Committees in other Divisions, especially Basic Science Division. A bibliography on glass structure has been proposed.

Standard Glass Committee—C. H. Hahner, chairman. Mr. Hahner said his committee desires to obtain better Standard Glasses free from straie and imperfections. The ultimate goal is a "bank" of simple glasses and to obtain fundamental properties of these simple glasses in order to improve knowledge of structure. The National Bureau of Standards will take a more active part in the participation of the Standard Glass Program.

International Glass Commission, Advisory Committee, H. R. Lillie, chairman, reported that the International Congress on Glass, will be held the first week of July at Paris, France. About fifty papers will be presented by authors from the United States, Great Britain, France, Belgium, Italy, Sweden, and the U.S.S.R.

The Gordon Conference on Glass will be held at the Kimball Union Academy, in Meriden, New Hampshire, this summer, August 27-31. This conference, held under the auspices of the American Association for the Advancement of Science, is carried out very informally without publication and the attendance restricted to 100.

(*Continued on page* 348)



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(*Continued from page* 336)

be deduced from the fact that a mixture of metakaolin and metallic silver can be oxidized in air at 1000°C and higher because such oxidation of the Ag to $Ag^+$ provides additional $O^{2-}$ ions which act as screeners for the $Al^{3+}$ ions.

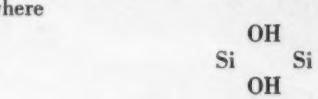
We may add to these examples a third one in which a system assumes temporary acidity. F. Hüttig's[27] "active intermediate state" corresponds to an incompletely reacted mixture which has the characterisic features of incompletely screened cations (hygroscopicity, adsorptive power for basic dyes from none-aqueous solutions). During the reshuffling of the ions, i.e., during the reaction of MgO with $Al_2O_3$ to form $MgAl_2O_4$, the system passes through a stage in which the cations are not as well screened as they are in the reactants or in the reaction product. Thus, if we want to call MgO a base and $Al_2O_3$ an acid, we must realize that this mixture has to go through a more acidic state before "salt formation" is completed.

These three examples may suffice to illustrate that the concept of acidity is inadequate when applied to solid state chemistry. Acidity was introduced originally in order to characterize a molecular species, e.g., HCl or $H_2SO_4$, when dissolved in water. Acidity and basicity was a convenient concept for describing the driving force of a chemical reaction, salt formation. This concept becomes artificial if we have to assume that a base reacting with an acid has to form a stronger acid first before it forms the salt.

## VI. ACIDITY OF THE CRACKING CATALYST

Our discussion on the possibility and the justification of extending the acid-base concept to the solid state would not be complete if it did not include a chapter on the cracking catalysts. "Cracking" is a process which changes certain fractions of crude oil into more valuable products. Originally the word "cracking" was used for the thermal breakdown of long chain paraffin molecules into smaller fragments of greater volatility. Today this process is used not only for changing the size of molecules but also for modifying their structures. "Cracking" as it is used today includes isomerization, alkylation, and even polymerization reactions. All of these reactions have one thing in common: they can be initiated by acids. Using the K. Fajans[2] quanticule concept we describe these reactions as initiated by the penetration of a proton into a $(\bar{e}_2)$ quanticule of a hydrocarbon molecule. This process changes the doubly negative charged link between two carbon cores into the singly charged $(\bar{e}_2\,H^+)^-$ or $H^-$ quanticule. Our interpretation of the role of protons in cracking of hydrocarbons treats isomerization and similar reactions on a par with the hydrothermal method which is used to catalyze the reaction of oxides.

Halides undergo solid state reactions at a much lower temperature than oxides. The main reason for their greater reactivity or lower activation energy is that the energy requirement for removing a $F^-$ or a $Cl^-$ ion from a cation is less than that required for removing a doubly charged $O^{2-}$ ion. Whereas a temperature of less than 500°C is sufficient for the reshuffling of the ions of two alkali halides, e.g., $KF + LiCl = KCl + LiF$, temperatures around 1000°C are required in order to react $SiO_2$ or $SnO_2$ with MgO or CaO. The reactions between these oxides, however, can be greatly accelerated by heating the mixture in an atmosphere of water under normal or, better, under a higher pressure (hydrothermal reactions). In this case the mechanism of the reaction is changed from the breaking of Si—O—Si bonds into one where



groups are reshuffled. The principle of the hydrothermal reaction is the changing of $O^{2-}$ ions into $OH^-$ ions by protons and making available additional screeners in the form of $OH^-$ ions.

In the same fashion a proton should lower the energy barrier for the regrouping of the $C^{4+}$ $(\bar{e}_2)$ $C^{4+}$ links of a hydrocarbon by temporarily changing them into $C^{4+}$ $H^-$ $C^{4+}$ links. The proton which penetrates the $(\bar{e}_2)$ quanticule may come from different sources, e.g., HF, $AlCl_3 + HCl$, $H_3PO_4$ or from certain solids which are called cracking catalysts. The chemical characteristics and the structure of cracking catalysts have been discussed by A. G. Oblad, T. H. Milliken and G. A. Mills[28]. This paper also gives numerous references to earlier work in this field.

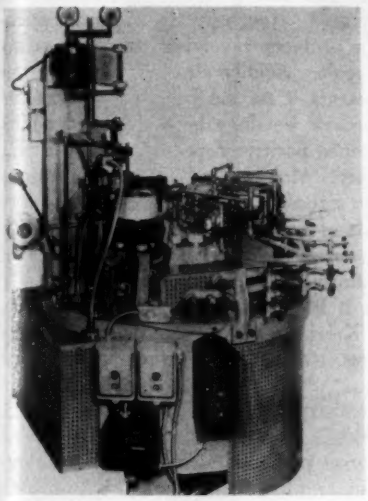
From a structural point of view the characteristic feature of this group of catalysts is the fact that they are composed of two oxides none of which alone has sufficient acidity to be a good catalyst. Calcined mixtures of coprecipitated $SiO_2$—$ZrO_2$ or $SiO_2$—MgO are catalytically active. They are strong acids at 400-500°C in spite of the fact that the coprecipitate of $Mg(OH)_2$ with silicic acid has distinctly basic properties when suspended in water. The most generally used cracking catalyst contains $Al_2O_3$ and $SiO_2$ and it makes little difference whether this catalyst is derived from the calcinations of certain natural clay acids or synthesized from sodium silicate and aluminum salts. Both processes involve removing of alkali and calcination of the ammonium salt of an alumino-silicic acid.

The question "Why has a combination of oxides a stronger acidity than either one of the components"? reminds us of the observations of G. F. Hüttig[27] or of W. Jander and associates[29] who found that systems such as ZnO—$Al_2O_3$ when reacting under formation of $ZnAl_2O_4$ go through an extremely "active intermediate state" (see Section V). G. F. Hüttig's[27] active intermediate state has the characteristic feature of being more acid than both the reactants and the reaction product.

The dehydration of $Mg(OH)_2$, $Al(OH)_3$, $Si(OH)_4$ and similar gels is a process in which these systems gain entropy through the formation of $H_2O$ molecules. Dehydration causes the anion to cation ratio to decrease and the cations of the system lose screening. They can improve their screening to a certain extent by arranging the anions in a more symmetrical fashion, e.g., by forming periclase or gamma alumina. When coprecipitated gels are heated they go through stages where the dehydration produces highly unscreened cations because the conditions do not permit crystallization to take place.

(*Continued on page* 346)

# New Equipment and Supplies



### MICRO-MINIATURE GLASS BODY MAKING MACHINE

Kahle Engineering Company, 1310 Seventh Street, North Bergen, New Jersey, announced the development of a new automatic micro-miniature glass body making machine, Number 2461. The machine produces, at a high speed, glass incapsulating bodies consisting of a micro-miniature bulb, open at one end, with a lead wire sealed in the other end. From start to finish, the machine completes its precision operations without attention. The automatic operations include glass beads and lead wire feeding; glass shaping, sealing; cutting wire with square ends; rotary wire-straightening; loading and unloading. All cutters that require sharpening and replacing are readily accessible for minimum down time. Exact tolerances on O.D.: length and concentricity are closely maintained and all parts subject to heat are constructed of heat-resistant alloys. More detailed information may be obtained by writing the company.

### BANTAM SIZE VIBRATOR

Martin Engineering Company, Neponset, Illinois, have developed a bantam sized vibrator for operation on steam or air. Vibrolator SAH-10 weighs only 4 ounces and it is claimed to be the lightest full-powered mechanical vibrator available.

It is designed for use on hoppers, feeders, molds, gauge panels, packaging machines, etc. Frequency of vibration is infinitely variable from 0 to more than 50,000 CPM. Operating pressure may vary from 5 to 150 psi. The vibrator is self-starting, self-cleaning, spark-proof and quiet in operation. A catalog describing this and 51 other vibrolator sizes and models for full range of industrial application can be requested from the company.

### ACCIDENT-PROOF BLAST-BURNER

Fisher Scientific Company, 498 Forbes Street, Pittsburgh 19, Pennsylvania, have announced an accident-proof, completely noiseless blast-burner. It has an almost unlimited range of flame sizes and temperatures. It incorporates such features as multi-flame design which enables one to select any number of flame sizes without changing tips when switching from one flame to another. Secondly, it is a silent operation as the gases are directed by channels in the burner body to a double ring of holes in the tip. Oxygen and gas are broken up into small streams and mixed externally. The external mixing of gases means no combustion in the burner body, no danger of back-flash when large flames are used, therefore, it is safe to use. There are a number of other features. The multi-flame burner can be used with any gas, and at normal gas pressures. A pilot flame keeps the burner always ready for use and the pilot flame size is controllable too.

### NEW GLASS SAW

The Hendrick Manufacturing Corp., Marblehead, Massachusetts, has developed a new automatic overhead-rail glass saw, Model MLS. The saw produces clean, straight vertical or bevel cuts in plate, bullet-proof and corrugated structural glass. Very narrow strips of plate glass may be cleanly cut from the original sheet without danger of crazing, to effect great reduction in finishing time.

The equipment consists of a saw carriage supporting a ¾ HP motor, mounted on 10 foot steel rails and activated by a lead-screw and half-nut system similar to a standard engine lathe, provided with a variable speed drive which is infinitely variable between 0 and 4′ per minute. The rails are raised and lowered by means of a bevel gear system and crank at the operator's end of the machine. The saw is provided with an adjustable limit switch which automatically shuts it down at the end of the cutting pass.

Water jets are provided for cooling the blade and, after proper coolant pressure and carriage travel speed have been selected, the operation is fully automatic and requires no further attention. The carriage is quickly retracted by means of a handwheel, chain and sprocket system, after the half-nut is disengaged from the lead-screw.

The saw has a capacity of 8½ feet and has a 3″ depth of cut with an 8″ blade. Standard glass saw blades with ⅝″ hole may be used. The rails may be quickly tilted to 45°. This permits accurate bevel sawing and opens new possibilities for structural glass.

The cost of the saw is moderate and it is expected to fulfill specialized requirements in the glass industry.

### ALL PURPOSE POLISHING KIT

Cratex Manufacturing Company, 81 Natoma Street, San Francisco 5, California has just developed a comprehensive, yet inexpensive polishing kit to meet the need of manufacturers to test and demonstrate Cratex rubberized abrasives on actual deburring, smoothing and polishing operations. This kit contains an assortment of 24 of the most popular Cratex polishing wheels, cones, blocks and mandrels which are in use in industry for cleaning and polishing molds, dies and castings, removing film, coatings and enamel, etc.

The kit contains complete instructions for efficient application and is sold at industrial supply dealers, or may be ordered from the company.

### NEW SPOT CHECK SURFACE THERMOMETER

Pacific Transducer Corporation, 11836 W. Pico Boulevard, Los Angeles 64, California, announces a new spot check surface thermometer. This thermometer, made entirely of stainless steel, with a range from 50° F. to 1000° F., is easy to read, compact and fast operating. The instrument is merely layed on the surface to be checked and within 60 seconds the thermometer reaches stability and the exact temperature can be easily read. It reads accurately temperatures of all surfaces, such as dies, furnace skins, boilers, cooled billets, etc. Besides the surface temperatures, it also reads ambient temperatures in furnaces, ovens and other enclosed spaces, as well as in non-corrosive liquids and gases, up to 1000° F.

The thermometer Model 573, is calibrated to within plus or minus 2 per cent and can be reset by the user, if necessary, at any time. The diameter is 1¾ inches overall, and it weighs 1/3 ounce.

(*Continued from page* 344)

There are local variations in the chemical composition and generally there is a lack of stoichiometry in the coprecipitate. This is the reason why the chemical properties of calcined mixed hydroxides can deviate strongly from additivity and produce surfaces which are extremely acid. Similar acids can be obtained when certain clay minerals are changed into "hydrogen clays" by base exchange and then calcined.

The extreme acidity of these phases expresses itself in the retention of water and as mentioned before (see Section V) it can lead to an unusual reactivity with metallic silver and oxygen. Normally, metallic silver cannot be oxidized by molecular oxygen because the rate of oxidation is very slow at room temperature and at higher temperatures silver oxide is not stable. A mixture of metallic silver with the pure single oxides, silica, alumina, or titania, shows signs of oxidation when heated in air to 1000°C. The maximum amount of $Ag_2O$ formed under these conditions varies with the nature of the oxide, but it is not more than a fraction of one per cent of the oxide present. The combination of alumina plus silica in the form of kaolin or the alumina silica catalyst, however, makes it possible to oxidize and stabilize as much as 30 per cent $Ag_2O$. I. Westermann[30] found that at 1400°C the reactivity of metallic silver with oxygen drops to practically zero in the presence of pure $SiO_2$ or $Al_2O_3$. In the presence of calcined kaolin, however, even at this high temperature a mixture containing 30 per cent $Ag_2O$ is stable.

Sir Humphry Davy (1814) once made a truly prophetic statement when he remarked that acidity does not depend upon any particular element but upon "a peculiar arrangement of various substances." The acidity of the alumina silica catalyst is purely structural and depends upon the unscreened conditions of a relatively small number of cations.

G. A. Mills, E. R. Boedeker and A. G. Oblad[31] found that in an active cracking catalyst the total number of sites which are active for the cracking of cumene is about $3.6 \times 10^{19}$ sites per gram or $1.2 \times 10^{17}$ sites per square meter of the accessible surface. These figures can be interpreted as if 4 per cent of the surface area is catalytically active.

This raises an additional question: "Why can water be retained by a combination of the two oxides so that the catalyst can donate protons at temperatures up to 500°C?" This question can be answered on the basis of H. von Wartenberg's[32] experiments on the volatility of $Al_2O_3$ in an atmosphere containing $H_2O$. At its melting point (2040°C), aluminum oxide gains entropy but the $Al^{3+}$ ions lose screening because the surrounding $O^{2-}$ ions are less symmetrical in the melt than they were in the crystal. For this reason $Al_2O_3$ at the melting point reacts with $H_2O$ in order to improve the screening of the $Al^{3+}$ ions by increasing the anion to cation ratio. The amount of water which is retained by an alumina silica catalyst at 800°C is of the order of 1 per cent. This water participates in the structure in the form of $OH^-$ ions. However, the proton can migrate from the $O^{2-}$ ion into the others and over a time average it will be found in the most polarizable $O^{2-}$ ions of the system.

## VII. SUMMARY

The concepts of "acids" and "bases" can be compared with the expressions "hot" and "cold" or with the positive and negative figures on a temperature scale. These expressions are inherited and they are convenient and will continue to be used. However, any rigorous scientific treatment of a problem involving temperature requires an absolute scale. Acidity also can be better understood if one presents it on the basis of an absolute scale. In our approach we describe a molecule which contains a well screened positive core, e.g., $CCl_4$ or $SF_6$, as having zero acidity. Molecules which contain cations in an incompletely screened condition, e.g., $SO_3$, are acidic. On the basis of our screening theory the acidity of a molecule is inversely proportional to its degree of screening. This definition makes it obvious that acidity is relative and that it is a function of the temperature. Analogous to the Kelvin scale, which does not have negative temperatures, we do not introduce bases in our definition of acidity.

For aqueous chemistry the acid-base concept of S. Arrhenius is very clear. The acidity of water is chosen arbitrarily as a neutral point and less acid systems are called bases. This system has its merits and we show in detail how the acidity or the basicity of aqueous solutions depends upon the cations which are introduced. Their charges, sizes, and electronic configurations are equally important.

Glass technologists attempted to do the same for glasses. Selecting a certain composition as a "neutral point" the concepts of acidic and basic oxides were introduced into glass technology. However, in contrast to aqueous solutions where the mobility of the proton equalizes the degree of screening within the whole system, glasses cannot be described by a single parameter which would be equivalent to the pH of a solution. Extending the acid-base concept to glasses leads to the paradoxical conclusion that CaO or MgO when introduced into alkali silicates and borates are stronger acids than $SiO_2$ or $B_2O_3$.

An explanation on a structural basis is given for the well known observation that the resistivity of an alkali silicate glass toward attack by acids can be greatly improved if oxides such as $TiO_2$, $ZrO_2$, $Ta_2O_5$, etc. are introduced.

The difficulty of retaining the acid-base concepts for crystalline solids is just as great as for glasses. It can be shown that the reactions between CaO and $SiO_2$ cannot be fully understood on the basis of salt formation. Silica can react with CaO beyond the formation of the orthosilicate.

The alumina silica catalyst is chosen as an example for the development of high "acidity" in systems which contain incompletely screened cations. This catalyst is only one example of the much more general acidity and reactivity of "intermediate states" which form when two oxides react and when the reaction has not gone to completion. The acidity of these amorphous solids cannot be characterized by one parameter because the degree of screening and the acidity of various lattice sites varies over a wide range. Sometimes it becomes desirable to neutralize the most acidic surface sites by alkali in order to direct the cracking into the desired course.

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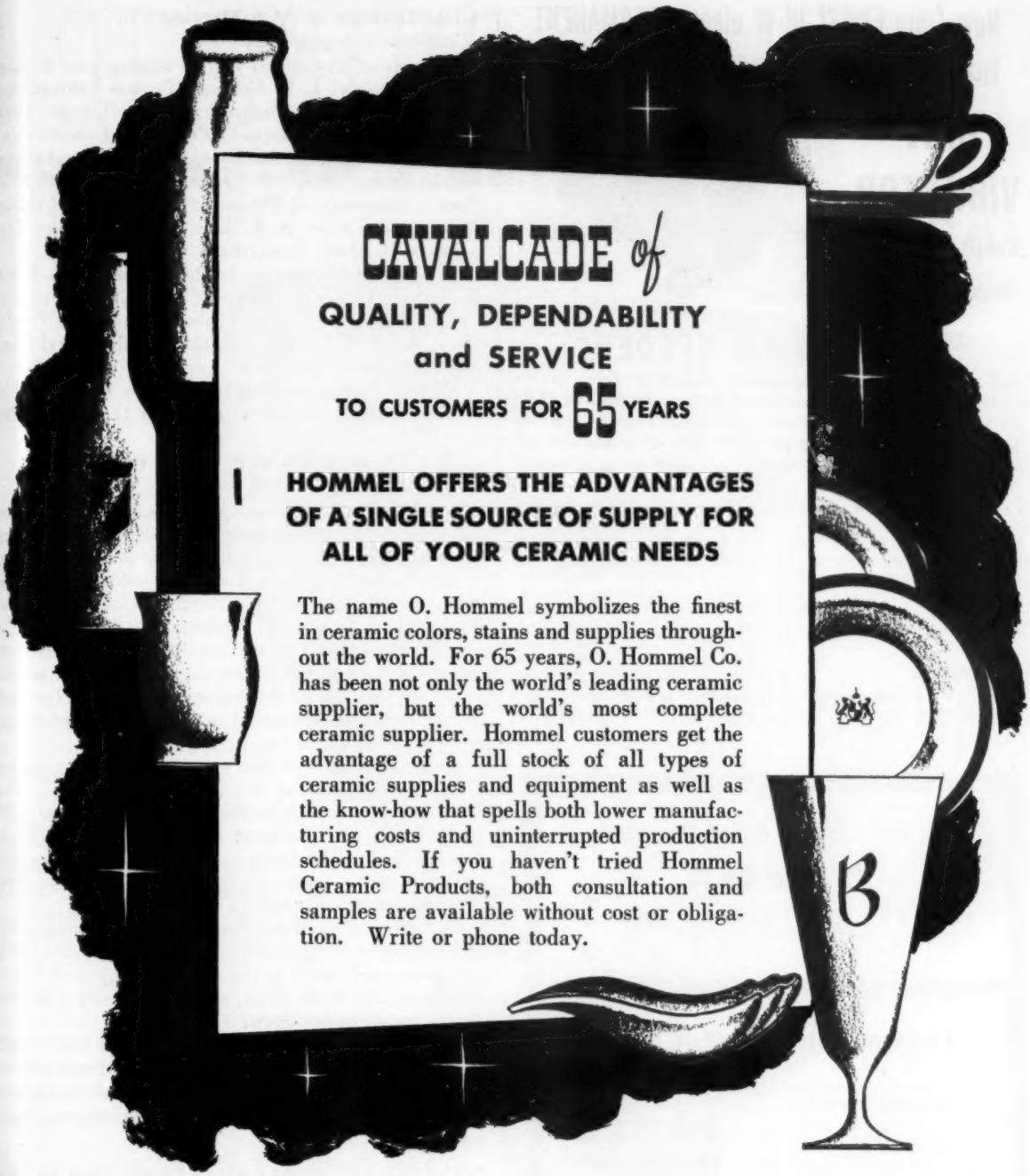

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## Glass Division of ACS Meeting . . .

(*Continued from page* 342)

Division officers elected for the coming year were as follows: Trustee: L. G. Gehring—Preston Laboratories, Butler, Pennsylvania. Chairman: J. Earl Duncan—Pittsburgh Plate Glass Company, Creighton, Pennsylvania; Vice Chairman: A. O. Anderson, Bell Telephone Laboratories, Murray Hill, New Jersey; Secretary: Fay V. Tooley, University of Illinois, 611 W. Oregon, Urbana, Illinois; Counsellor: A. K. Lyle, Hartford-Empire Corporation, Hartford, Connecticut.

The Program Committee for the coming year is Frank R. Bacon, Chairman, Owens-Illinois Glass Company, Toledo, Ohio; R. K. Day, Libbey-Owens-Ford, Toledo, Ohio; and J. R. Hensler, Bausch & Lomb Optical Company, Rochester, New York.

The Fall Meeting of the Glass Division will be held in Bedford Springs, Pennsylvania, October 11 and 12, 1956.

## O-I ANNOUNCES NEW GLASS CONTAINER PLANT

Owens-Illinois Glass Company announced that it is starting construction of a new glass container manufacturing plant in Atlanta that will be the largest in the Southeast. It will service a market area that includes Alabama, Florida, Georgia, North and South Carolina, Tennessee, Mississippi and parts of Louisiana.

Preliminary work on the 85-acre site in the Atlanta suburb of Hapevill has already begun. The plant will be equipped with two of the largest glass melting furnaces in the U.S. glass industry, each capable of producing more than 200 tons a day.

A feature of the new plant's design is the provision for complete ventilation of the manufacturing area. The two furnaces will each be located in separate 100 x 80 foot extensions on the south end of the main building. The building wall enclosing most of the furnace area will be open at the bottom to permit outside air to flow into and through the furnace working areas.

The plant's sidewall construction will be a combination of brick and corrugated asbestos in the warehouse, brick and corrugated metal in the manufacturing area, brick and glass block in the shops, and flat glass and porcelain enamel panels in the offices.

Scheduled for completion in the summer of 1957, it will employ between 300 and 400 at the outset, and will be capable of producing about 300,000,000 glass containers annually for the packaging of foods, beverages, drugs and chemicals.

## MANAGEMENT PERFORMANCE OF TWO GLASS MANUFACTURERS TERMED OUTSTANDING

Outstanding performance in vital management areas has drawn praise for two glass manufacturers, Corning Glass Works and Owens-Illinois Glass Company.

The 1956 Manual of Excellent Managements, published by the American Institute of Management, singles out these two firms from among 409 companies it lists as deserving particular merit for excellence in one (or more) of the Institute's areas of management appraisal. Both companies are cited for carefully planned and fruitful research and development activities.

Owens-Illinois is also cited for its soundness of internal procedures and lines of communications.

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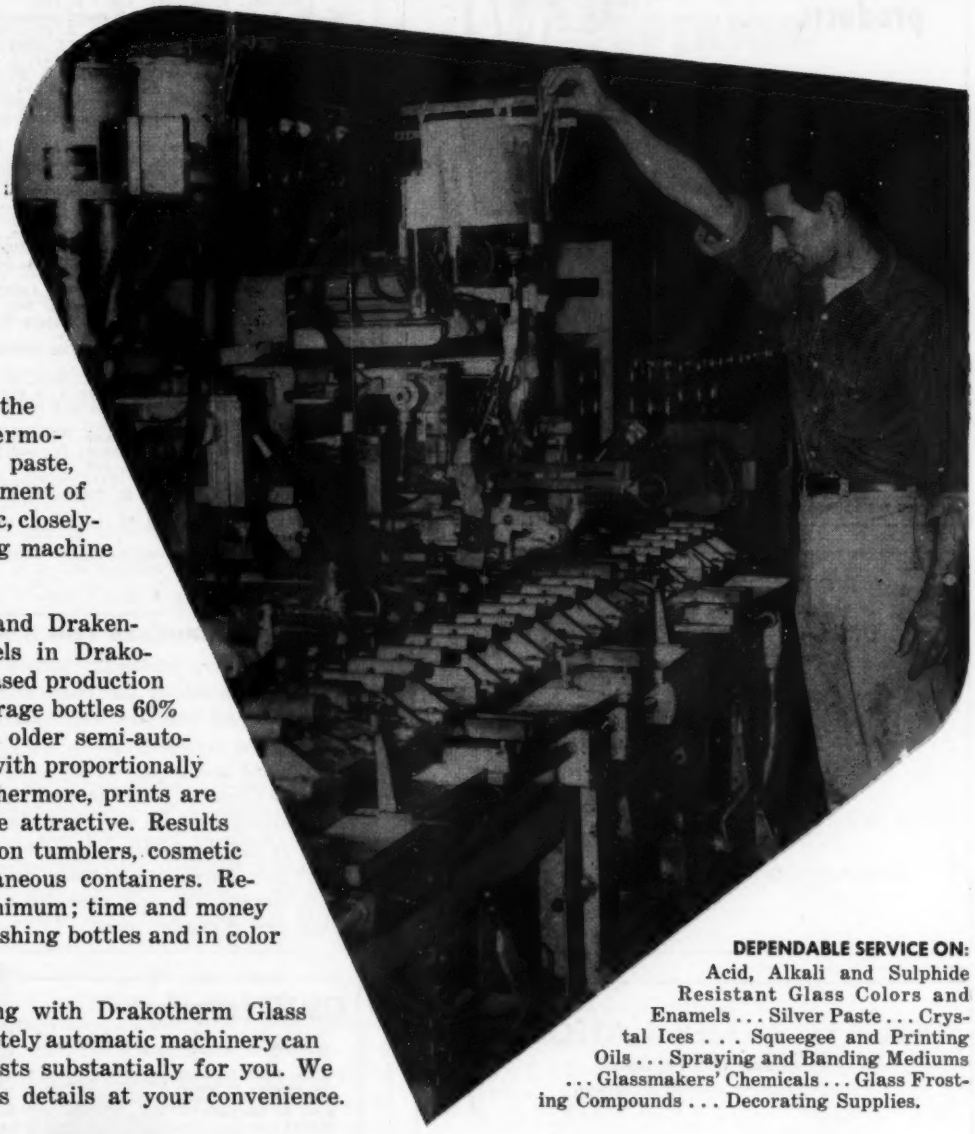

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## Acid Base Relationship . . .

(*Continued from page* 346)

### REFERENCES

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### NEW WAREHOUSES FOR ANCHOR HOCKING

Wm. V. Fisher, president, Anchor Hocking Glass Corporation, announced the construction of new, modern type steel and concrete warehouses at its Salem, New Jersey glass container plant, its Connellsville, Pennsylvania plant and at its wholly-owned subsidiary plant—Tropical Glass & Box Company, Jacksonville, Florida. Construction on both the Connellsville and Jacksonville plants is slated to start immediately.

The new warehouse at Salem will be ready for occupancy August 1st, and provides an additional 40,000 square feet of storage space.

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## Vacuum Fabricated Glass . . .

(*Continued from page* 324)

dividual mandrels which have a cross section that may be round, square, hexagonal, octagonal, triangular, or flat. Lengths of metal rods in these shapes are commercially available as stock items. An unlimited number of complex internal shapes in glass tubing may be produced by combining straight sections of these metal shapes (See Figure 5). The group of mandrels used to form a pattern are held together at each end by wire or screws. Graphite coating may be applied to the individual mandrels or the composite may be dipped after assembly. Mandrel patterns previously considered impractical due to prohibitive machine shop charges, may now be obtained by this method at relatively low costs.

### Glass Tubing

Preliminary inspection of glass tubing for the selection of size and the elimination of imperfections is essential. Flaws such as 'stones' (crystalline contaminations) and 'blisters' (large bubbles) should be rejected. Air lines within the wall of the tubing, which may produce isolated air bubbles in the softened glass, should be rejected.

To assure uniform wall thickness and a smooth outside diameter, the glass tubing size should be a close fit to the mandrel. Tubes which fit too tight often crack as the temperature of the higher expanding mandrel rises. Oversize tubing will produce a 'fold-over' effect which has no aesthetic value, is difficult to anneal, and weakens it.

The tolerable size differential is cited in the following example. For a mandrel having a diameter of one quarter of an inch, the tubing inside diameter should not exceed the mandrel by more than 0.030 inch for best results. Glass tubes with an I.D. as much as 0.075 inch greater than the mandrel may be used if the mandrel is axially centered by the use of shims or dimpling the glass. Larger tubing needs additional shrinking on intermediate size mandrels, redrawing the glass tubing or performing by methods familiar to the art of glassworking.

### Vacuum Required

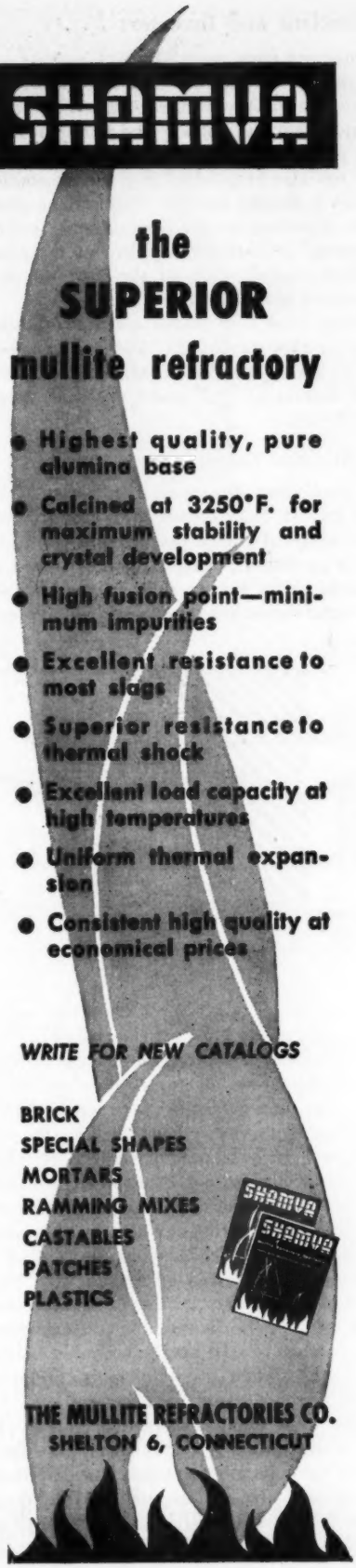
A partial differential in atmospheric pressure suffices to collapse the softened glass over a mandrel. It has been found, however, that the lowest practical attainable pressures are to be desired for the elimination of mandrel oxidation, sticking, and precision control. Vacuum in the order of $10^{-2}$ millimeters of mercury and better is easily attained with most mechanical forepumps (Figure 6). To overcome minute leaks and rapidly remove moisture and occluded gases, a backer pump with a pumping speed of better than 25 liters per minute should be selected. Diffusion pumps and vacuum gauges are not necessary, but a high frequency spark coil should be available. Heat for shrinking the glass should not be applied until the purple-pink nitrogen glow has disappeared, as seen by the use of the spark coil.

In order to rotate the glass tube and still maintain a good vacuum, an effective vacuum swivel must be used.

### Recent Developments

The fundamentals of vacuum forming glass tubing An example of a good vacuum swivel is shown in Figure 7. Swivels may be purchased commercially or constructed using a Wilson Type seal or 'O' ring shaft seal.

(*Continued on page* 354)



## Inventions and Inventors . . .

(*Continued from page* 333)

the same invention. The same holds for the other phosphates which may be used. It is more advantageous to form these in the wet way and finally melt down the reaction product.

It has also been found that for the stabilization of the glasses a smaller amount of aluminum phosphate or indium phosphate is very advantageous, not only in that it increases the chemical stability of the glass but it also hinders crystallization of the melt during clarification at lowered temperatures.

There were four claims and the following references cited in this patent: 1,654,404, Blumenberg, Dec. 27, 1927; 2,518,194, Silverman, Aug. 8, 1950; 585,257, Great Britain, of 1947, and *Sprechsaal:* August 15, 1918; pp. 149-150.

### Feeding and Forming

*Glass Rolling Apparatus. Fig. 3. Patent No. 2,723,931.* Filed July 31, 1953. Issued November 15, 1955. One sheet of drawings. Assigned Ford Motor Co. by H. L. Mercer.

This invention is particularly concerned with the construction of the rubber rolls in which curved laminated glass sandwiches are deaerated and prepressed.

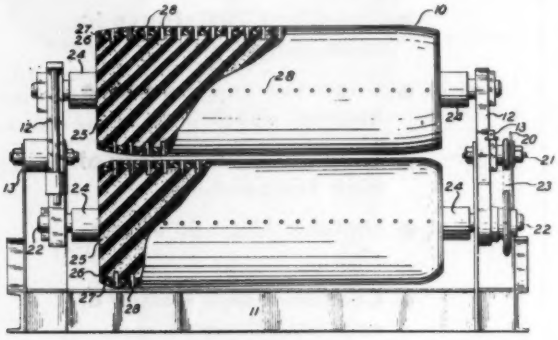


Fig. 3

The preferred rolls for deaerating and prepressing curved glass sandwiches are shown in Fig. 3. They comprise an upper floating roll 10 and a lower driven roll 11, journalled for rotation in side members 12. Side members are in turn journalled for rotation in trunnions 13. Trunnions 13 are located intermediate the axes of upper floating roll 10 and lower driven roll 11. Lower roll 11 is driven through sprocket 20, which is mounted on stub shaft 21. This sprocket 20 and stub shaft are arranged to be chain driven from any convenient source of motion (not shown). Shaft 22 which is coaxial with lower driven roll 11, is driven by a chain 23. Upper floating roll 10, is driven only frictionally by contact with lower driven roll 11. If desired, the journals supporting the upper floating roll 10 maybe slideably mounted in side members 12, so that gravity alone is effective to maintain this roll in contact with the lower roll.

It has been found in practice that the breakage of glass in the rolling operations can be substantially reduced if the rolls are constructed as described.

There were five claims and the following references cited in this patent: 2,191,144, Hornbostel, Feb. 20, 1940, and 2,288,675, Berry, July 7, 1942.

### Glass Wool and Fiber

*Glass Fiber Product. Patent No. 2,723,215.* Filed May 31, 1950. Issued November 8, 1955. Two sheest of drawings. None reproduced. Assigned to Owens-Corning Fiberglas Corporation by L. P. Biefeld and W. K. Lydic.

The invention finds particular utility in the manufacture of glass strands and yarns of the continuous-type. These are made by drawing out streams of molten glass, without interruption, into continuous filaments which are gathered together as they are formed in a strand. The strand is made up of a compact bundle of fine filaments, all extending in side by side relation and continuously throughout any normal length of strand.

A molten coating material is applied to glass filaments as they are formed. The material is applied to the individual filaments before they are gathered together into a strand. The molten material may be deposited on the filaments in large quantities. They provide a substantial coating on the fibers in order to effectively protect the fiber surfaces against abrasion and make the resulting strand or yarn considerably more durable. As the filaments are gathered together into a strand, the coatings on adjacent fiber surfaces coalesce to weld the filaments together into a well bonded highly integral bundle and thereby cause all the filaments to act together to resist stresses, rather than being loaded unequally. As a result, the tensile strength of the strand is greatly increased.

When applied in molten condition to the individual glass filaments as they are formed, it is possible to secure deposition of the protective coating in amounts ranging from 10 per cent to 30 per cent and even more by weight, quantities which were impossible to achieve in a manner that provided uniform distribution of the coating material through the cross-section of the strand.

Suitable compositions of coating materials for application to the filaments in the manner described are as follows:

Example 1: 99 per cent paraffin
1 per cent diallyl diethoxysilane

Example 2: 98 per cent paraffin
2 per cent methylphenyl polysiloxane

Example 3: 99 per cent ozokerite
1 per cent octadecylamine

Example 4: 98 per cent paraffin
1 per cent diphenyl polysiloxane
1 per cent of the reaction product of tetraethylene pentamine and stearic acid

There were 8 claims and the following references cited in this patent: 609,452, Morris, Aug. 23, 1898; 1,421,306, Rawlings, June 27, 1922; 2,224,274, Powers, Dec. 10, 1940; 2,234,986, Slayter et al., Mar. 18, 1941; 2,333,535, Lauer, Nov. 2, 1943; 2,392,805, Biefeld, Jan. 15, 1946; 2,547,396, Joanen, Apr. 3, 1951; 2,550,438, Zoeller, Apr. 24, 1951, and 2,582,037, Hyde, Jan. 8, 1952.

*Making Mineral Wool. Patent No. 2,728,949.* Filed October 21, 1949. Issued January 3, 1956. No drawings. Assigned Aquex Dev. and Sales Corp. by E. W. Sweet.

According to the present invention, a stream of molten siliceous material is subjected to a blast of steam to disrupt the siliceous materials into fibres, the steam containing entrained therein, a compostion comprising a thermo-

(*Continued on page* 358)

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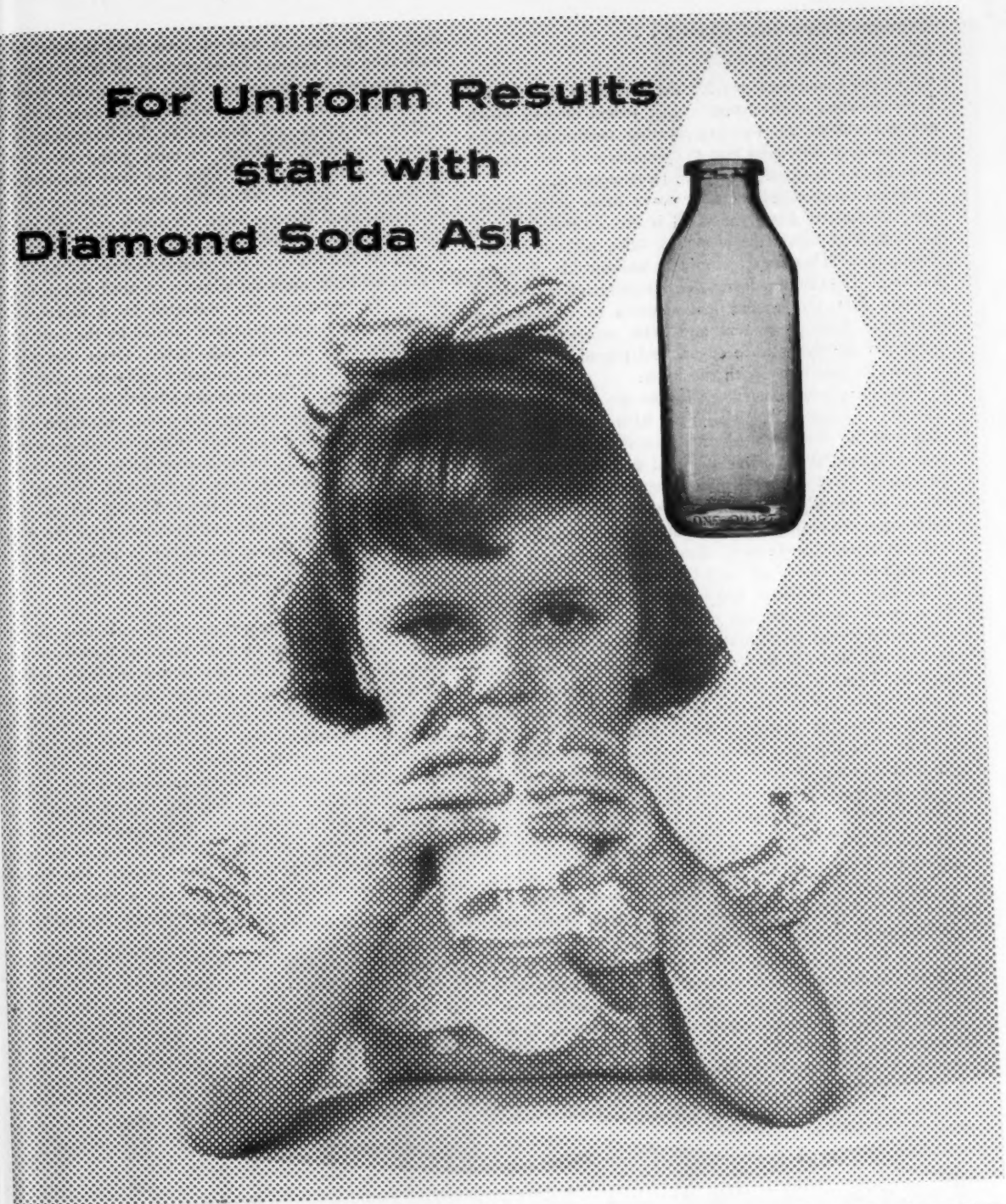

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## Vacuum Fabricated Glass . . .

(*Continued from page* 351)

have been given and provide the necessary background for diversified applications. Some recent devices which are a result of the vacuum forming technique will be reviewed. It is evident that the potentials of this process as a 'tool of research' are yet to be recognized.

In the construction of microwave tubes (See Figure 8A), conditions would be ideal if the wire helix could be suspended within the electronic tube, without contact or support. This would eliminate undesirable dielectric loading. The vacuum formed clover pattern fluted tubing (Figure 8B) was a practical solution to this support problem. Axial alignment and helix support were obtained by the three knife edges, and placed a minimum of glass in proximity with the helix.

The tubing was constructed by the use of a compound mandrel (Figure 8C). Fine glass fibers and rods were placed in the crevices formed by the three-steel mandrel rods (Figure 8D). It was essential that the finest fibers be placed in the grooves first because of the reluctant effects of the high viscosity softened glass to assume knife edge projections at practical working temperatures and pressures. These strong fibers and rods ranged from a few thousandths of an inch to twenty-five thousandths of an inch in diameter, and were made in long lengths from small balls of molten glass. To simplify assembly and assure proper positioning, the glass and steel rods are tied at both ends, in grooves provided on each mandrel, with two turns of fine Kovar wire. The low expansion Kovar wire further assures tangential contact of the higher expanding mandrels when heating takes place. Shrinking of the tube proceeds in the same manner as described, using the glass lathe or electric oven.

### Glass Powder Technique

Glass powder of the same glass as the outer tube may be used as a filler and is preferred to the fibers for filling voids and retaining a round outside diameter. Powdered glass techniques usually produce translucent or opaque glass products due to millions of trapped air bubbles. Vacuum formed tubing, processed with powdered glass, possesses the inherent advantage of being transparent because all air and moisture have been removed prior to fusion. The conditions necessary for perfectly dense transparent tubing are: (1) Vibration—a compacting process for powders. (2) Vacuum—to remove all traces of air and other gases. (3) Heat—to drive off moisture, collapse the tube, and fuse the powder and outer tube into a homogeneous mass.

These requirements are conveniently incorporated into the machine shown in Figure 9. The tube holding rack is constructed from a refractory material which is anchored to and supported by the table of an electric vibrator. The vibrator is of the type used for agitating sieving trays. A stationary electric oven, controlled by Variacs, houses the refractory rack but does not contact the vibrator table. Long glass test tubes containing mandrels are placed in the rack and the tubes are partially filled with glass powder. The vibrator is activated and the electric oven is switched on and held at 250° C. Powder is added in small quantities to each tube in succession, then repeated, until all tubes are filled to within an inch of the top. A wad of glass wool is inserted into each tube and vacuum hoses coming off from a manifold are attached to the tubes. This preliminary treatment prevents powder 'bumping' which causes loss of material within the tubes and damage to the forepump by the abrasive powder. As the vacuum pump removes the gases from the vibrating tubes, the oven temperature is increased to 550° C. (below the glass collapsing temperature) and held for one hour. A spark coil will indicate the absence of water vapor and air. The vibrator is turned off and the oven temperature increased to 740° C. —then held for about 10 minutes or until fusion is complete. Temperatures are indicated by a thermocouple placed within the annual space formed by the bore in the refractory rack and the glass tube. Oven controls are set at low heat so as to gradually cycle the tubes below the strain point. The tubes are allowed to cool to room temperature with the vacuum forepump operating. These temperatures are for Corning's Code No. 7052 glass and diameters of about ¼ inch. Kovar tubing mandrels were used which were later dissolved out in acid. Coated mandrels cannot be used, since the scrubbing action of the abrasive glass powder, when vibrated, removes the graphite, causing it to become imbedded in the fused glass.

### Glass Screw Threads

Standard fine and coarse screw threads may be produced in glass by the vacuum forming technique (See Figure 10). These glass threads are produced with so high a degree of accuracy as to be interchangeable with stocked metal screws or lathe turned screws. Glass-metal screw thread combinations have been used for rotating shaft seals, demountable vacuum tight connections with rubber washers and other hermetic closures. Considerable torque may be applied and full rubber compression for vacuum tightness achieved, well in advance of glass fracture. Screw threads in glass are produced by using a mandrel made from a stock steel screw. The threads are turned down so as to leave only a shallow helical

(*Continued on page* 356)

**Fig. 10. Standard fine or coarse screw threads can be vacuum formed into tubing for attaching to auxiliary metal apparatus or for demountable hermetic closures.**

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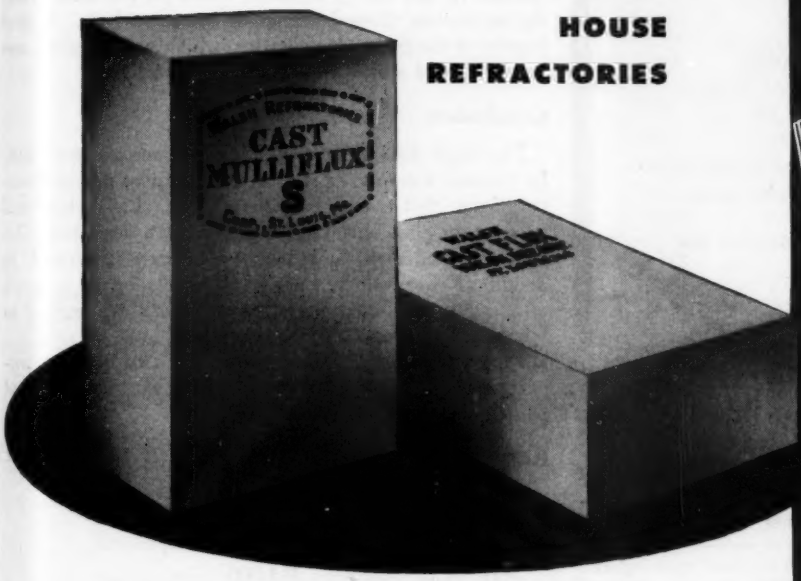


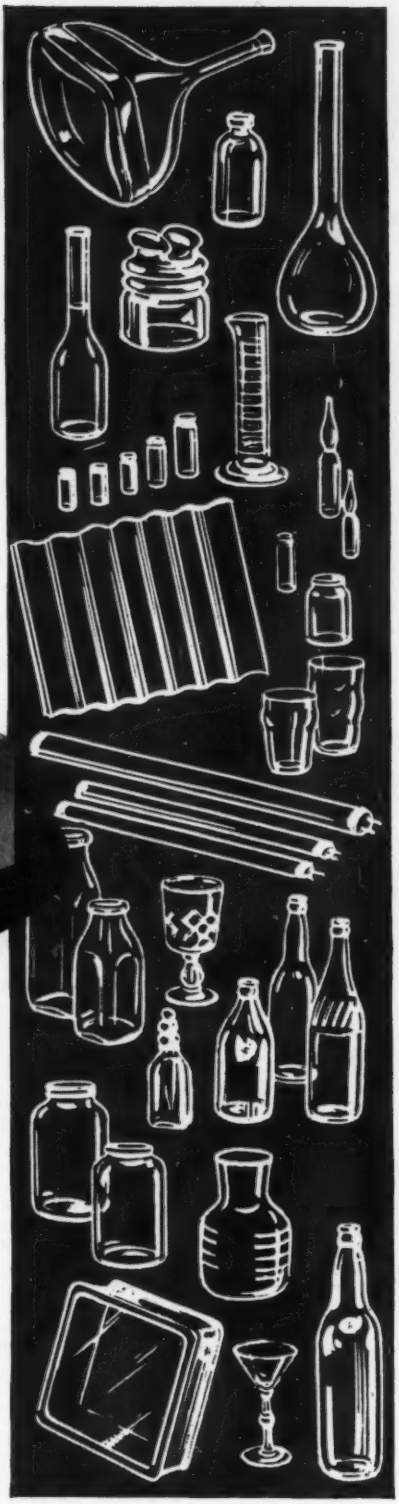

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### HAZEL ATLAS ELECTS OFFICERS

The board of directors of Hazel-Atlas Glass Company, Wheeling, West Virginia, elected J. H. McNash chairman of the board and president. Mr. McNash, formerly the chief executive officer of the company, was relieved of the duties of that office at his request.

H. G. Lewis, who has been vice president and secretary, was elected executive vice president. Norman G. Ross, formerly treasurer, was elected secretary-treasurer. George R. Worls was elected assistant treasurer and Jack W. Conkel, assistant comptroller.

## Vacuum Fabricated Glass . . .

(*Continued from page* 354)

groove. A wire, of glass sealing metal, is tightly wound in this guide groove and attached at both ends by small screws. The diameter of the wire is determined by the amount of stock removed from the screw. The overall diameter of the wire wound mandrel, is therefore, equal to the diameter of the original screw thread.

Standard glass shrinking procedures are employed. The glass tubing should be heated just enough to cause collapsing without excessive softening. Upon cooling, the mandrel is screwed out leaving the wire attached to the glass tube. Wire removal is accomplished with aqua regia, or, when dimension allowances have been provided, the wire may be left sealed to the tube. Screw threads, formed by the use of diamond cross section wire, yield the equivalent shaped thread of a tapped hole. Coiled inserts of diamond shaped wire, which can be used, are made of steel and are commercially available.

### Conclusion

The high accuracies and other advantages attainable by vacuum forming, as well as the pertinent patent literature from 1903 to date have been given. Laboratory and production glass shrinking methods were described. The required materials and techniques were reviewed in detail. New products have been developed as a result of vacuum forming. Their constructions are unique to the art of glassworking and include:

Precision knife edge microwave helix supports, transparent bubble free glassware by the use of powdered glass, and glass screw threads.

### References


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(2) U. S. Patent— 845,413
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(4) U. S. Patent—2,384,800
(5) U. S. Patent—2,377,861
(6) U. S. Patent—2,441,350
(7) U. S. Patent—2,532,091
(8) U. S. Patent—2,613,479
(9) Private Communication, Wilmad Glass Co., Landisville, N. J.
(10) Precision Glass, Fabrication and Uses
O. H. Graver and W. Conway
Paper presented at the 58th annual meeting of the American Ceramic Society, April 25, 1956.


### C. E. FRAZIER HONORED

On March 22, C. E. Frazier, chairman of the board of Frazier-Simplex, Inc., was honored by having bestowed upon him the Natl. Soc. of Prof. Eng. Award for contributions to the engineering profession.

Mr. Frazier is a Fellow of the American Ceramic Society and of the Society of Glass Tech. of England.

● The resignation of F. K. Rodewald from the board of directors of the Thatcher Glass Manufacturing Company, Inc., Elmira, New York, was announced by Franklin B. Pollock, the company's chairman of the board and president. The resignation became effective April 30, 1956.

No immediate announcement was made as to filling the Thatcher Board vacancy.

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## Inventions and Inventors . . .

(*Continued from page* 352)

setting resin, a mineral oil and a water-insoluble wax-like substance selected from the group consisting of waxes and heavy metal salts of the higher fatty acids. In a now preferred embodiment, the waterproofing composition is added to the steam in two parts, one of the parts comprising an aqueous dispersion of the resin, the other comprising the oil and wax-like substance, both being mixed with the steam prior to its contact with the molten stream of siliceous material.

The waterproofing materials employed in the process comprise a thermosetting resin, a mineral oil and a wax-like substance. For the thermosetting resin there may be employed a phenolformaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin, alkylated urea-aldehyde resins and alkylated melamine-aldehyde resins, thiourea-aldehyde resins, glyoxal and the like. For the mineral oil, there may be employed any mineral oil of high viscosity, but preferably an oil which has a flash point above 400°F. A suitable oil is a paraffin base saturated hydro-carbon oil derived from petroleum. The water-resistant ingredient comprises a water-insoluble soap, such for example, as soap formed from a higher fatty acid and a heavy metal such, for example, as zinc stearate, aluminum stearate, magnesium palmitate, and calcium stearate.

There was 1 claim and 11 references cited.

*Forming Mineral Fiber. Patent No. 2,729,849.* Filed Nov. 17, 1951. Issued January 10, 1956. One sheet drawings. None reproduced. Assigned to ¼ Midwest Insulations, ¼ Industrial Products Co., ¼ Carney Co., ¼ Airseal Insulations, Inc. by R. M. Downey.

The object of the invention is to provide means for a single large stream of molten mineral substance to be distributed uniformly upon the exterior surface of a vertically rotating disc or platter, to form on said exterior surface a relatively thin film of the molten material which, by the rapid rotation of the disc or platter, is disintegrated and forcibly directed off the peripheral edge of the disc tangentially and thereby broken up into fibrous streams. At the same time, directly across these fibrous streams of tangentially directed material, there is directed a jet or jets of fluid under pressure, preferably steam, which jets may cause to rotate at approximately the same velocity as the tangentially stream and substantially in the same direction.

The rotating disc onto which the molten material is directed is cooled by the effect of steam or fluid providing jet streams.

There were 7 claims and the following references cited in this patent:65,339, Butcher, Jr. et al., June 4, 1867; 687,524, Fellner, Nov. 26, 1901; 1,051,844, Passow, Jan. 28, 1913; 1,834,687, Davis, Dec. 1, 1931; 2,318,244, McClure, May 4, 1943; 2,328,714, Drill et al., Sept. 7, 1943; 2,470,569, Meighan et al., May 17, 1949, and 2,587,710, Downey, Mar. 4, 1952.

### PALLET REPAIR MANUAL

The most economical methods of repairing wooden pallets used with materials handling equipment in the Armed Forces has just been released to industry through the Office of Technical Services U. S. Dept. of Commerce.

Prepared by the Navy, the report includes information on the 48″ by 72″ stevedore pallet, the 48″ by 48″ pallet and the 40″ by 48″ pallet, both the block type and the four stringer type. Examples of types of damage which cannot be economically repaired are illustrated. Also included is a method of converting the 48″ by 48″ pallet to a 40″ by 48″ pallet for use with the straddle type fork truck and methods of cutting the block type and the stringer type for adaptation to the straddle truck.

Repair and modification techniques recommended in the manual are based upon a study of the methods employed at the Naval Supply Depot, Bayonne, N. J., and the Naval Supply Center, Norfolk, Va.

The report is PB 111755 *Pallet Repair Manual*, H. A. Rothe and M. Toscano, Naval Supply and Development Facility, Bayonne, N. J., Apr. 1955, 34 pages. It may be ordered from OTS, U. S. Department of Commerce, Washington 25, price $1.

### NBS ANNOUNCES NEW PUBLICATION

The National Bureau of Standards, U. S. Department of Commerce announce a new publication.

*Guide to Instrumentation Literature* by W. G. Brombacher, Julian F. Smith, and Lyman M. Van der Pyl, National Bureau of Standards Circular 567, issued December 14, 1955, 156 pages, $1.00. (Order from Government Printing Office, Washington, D. C.)

This circular is intended to assist research investigators, instrument users, and others interested in utilizing the extensive and scattered literature of instrumentation. It was prepared as part of the program of instrumentation research and development which is cooperatively sponsored at the National Bureau of Standards by the Atomic Energy Commission, the office of Naval Research, and the Air Research and Development Command.

Over 1200 references are listed, including abstract journals, bibliographies, 660 books on technology, directories of manufacturers, guides to and indexes of technical literature, periodicals of interest, and guides to dissertations, patents and specifications. Articles published in periodicals are not referenced, but indexes and abstracts of such articles on a given subject are indicated in the subject index. (NOTE: Foreign remittances must be in U. S. exchange and should include an additional one-third of the publication price to cover mailing costs.)

### SPECTACLE LENS TESTER

With the aid of an instrument developed by the National Bureau of Standards, it is now possible to measure both central and marginal powers of a spectacle lens with accuracy. This instrument, known as the Spectacle Lens Tester, was designed by Dr. F. E. Washer of the NBS staff in connection with a study[1] of eyeglass lenses for the Veterans Administration.

In operation it simulates the refractive effect of the various parts of the lens under study upon the human eye. Although the Spectacle Tester is basically a research tool, its essential principles have been utilized to design marginal-power attachments[2] for the standard vertex-power instrument used by practicing opticians.

(1) For further technical details, see instrument for measuring marginal power of spectacle lenses, by Francis E. Washer, *J. Opt. Soc. Am.* (in press).

(2) For further technical details, see A simplified method of measuring the marginal powers of spectacle lenses, by Francis E. Washer, *J. Reserach NBS* 55 (1955) RP 2607.

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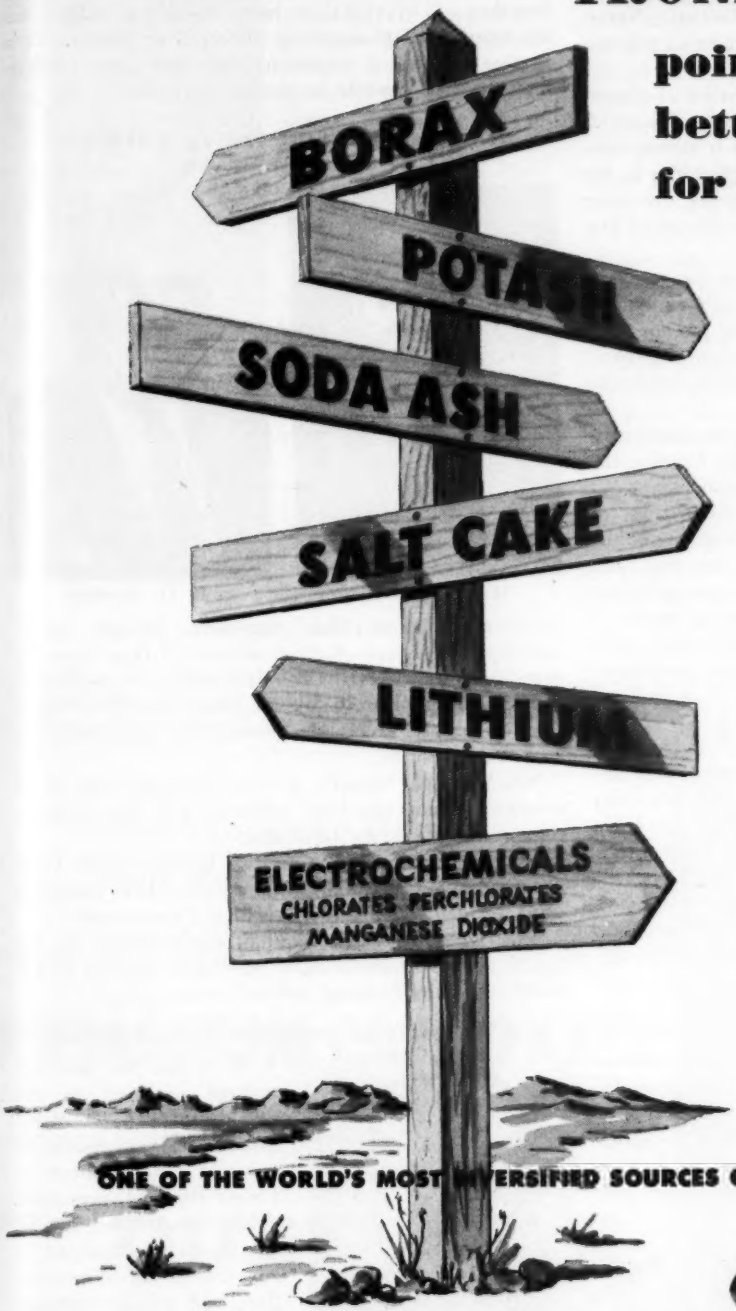


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**Research Digest . . .**

(*Continued from page* 334)

give accurate, as well as rapid results, the usefulness of these techniques to the glass analyst is limited. Nevertheless, a number of interesting studies are being pursued which may have value in the future.

The study of the absorption characteristics of glasses has been confined mainly to the wavelengths below 1.2 mμ for absorption in the infra-red region is almost complete at normal specimen thicknesses. Difficulties in the regions of longer wavelength are now being overcome by the application of techniques involving the use of fine powders on their films.

The powder technique is being used in the study of glasses and of glassmaking materials, such as quartz, calcite, dolomite and orthoclase. Up to the present time, the method has been used in the identification of mineral rocks and it has been reported that semiquantitative standards have been achieved.

In the thin film technique the absorption characteristics in the infra-red region are studied by blowing the glass into a film which is only —5 microns thick.

Studies of interest to the analyst in the regions of shorter wavelength have been concerned with the oxidation-reduction ratios of elements such as iron and chromium. It has been possible, for example, to assess the relative amounts of ferrons-ferric iron in glasses of relatively simple composition. The value of such work is not so much in the provision of a rapid method of analysis, as contributing to the solution of a problem which chemical analysis has not yet solved.

The application of colorimetric methods to the analysis of glass and glassmaking materials has been well established for many years and several of these methods form an integral part of normal analytical practice. The basis of colorimetry is the addition of a selective reagent to a solution of the sample, to produce a color which is characteristic of the element for which analysis is being made, the intensity of the color which is characteristic of the element for which analysis is being made, the intensity of the color being proportional to the concentration of that element. The intensity of color is then compared with that produced by standards, or the absorption at a selected wavelength is measured spectrophotometrically and a quantitative evaluation is made. In the early stages of these methods comparison was visual, but the development of absorptiometers and spectrophotometers has given considerable impetus to their applications and the uses to which they have been put have been extended.

As chromatography is essentially analytical, it must have considerable interest for the glass analyst. It provides another example of the recent application to present-day problems of a principle which was known in the last century.

The use of different "supports" or columns provide a convenient classification into three main categories—absorption, ion exchange and partition chromatography. These processes are often inter-related and all provide means of separation of various ions in a way which can be used to simplify analysis, for example, by removal of interfering ions.

The development of these techniques and their application to analysis is so recent that although some of them have been applied to silicate analysis, it has not yet been possible to test them sufficiently to establish their value for the industrial analyst, nor is there any evidence that they will provide more rapid methods of analysis for the more usual glassmaking materials or glasses. It is in the removal of interfering ions that these methods show the most promise for the glass analyst.

## NEW VICE PRESIDENTS AT AMERICAN WINDOW GLASS

H. W. McIntosh

H. D. Menoher

American Window Glass Company, in the regular meeting of its board of directors, elected three new vice presidents: they are H. Dean Menoher, vice president—manufacturing; Harold W. McIntosh, vice president—technical; and Francis M. Hernan, vice president-secretary and treasurer.

Mr. Menoher, formerly general superintendent of all company plants, has been affiliated with the company since 1909 in various capacities.

Mr. McIntosh joined American Window Glass Company in 1945 as assistant to the president, later becoming manager of the company's Technical Departments.

Mr. Hernan recently came to the company in the capacity of secretary-treasurer, and will continue in his position of chief financial and accounting officer.

## T. E. SNYDER APPOINTED AT O. HOMMEL

T. E. Snyder has been appointed assistant to the president of The O. Hommel Company, according to a recent announcement by Ernest Hommel, president.

Mr. Snyder, will be in charge of the company's advertising, sales promotion, and public relations activities and will assist the president in sales and administrative duties, and in the marketing activities of the O. Hommel Company, Carnegie, Pennsylvania.

Mr. Snyder, who previously was manager of advertising and sales promotion for the Exide Industrial Division of The Electric Storage Battery Company, Philadelphia, returns to Pittsburgh, where he was formerly executive director of the Pittsburgh area chapter with ACES, Americans for the Competitive Enterprise System, Inc.

## COLUMBIA-SOUTHERN APPOINTS E. W. HALEY

Appointment of E. Wayne Haley as assistant to the president of Columbia-Southern Chemical Corporation has been announced by E. T. Asplundh, president. Columbia-Southern is a wholly-owned subsidiary of the Pittsburgh Plate Glass Company. Mr. Haley has also been elected a vice president and director of the Pittsburgh Plate Glass Export Corporation.

As assistant to the president of the company, Mr. Haley will headquarter at their New York Office, located at 579 Fifth Avenue, and will have charge of the exportation of chemicals through either Columbia-Southern or PPG Export Corporation as well as handle other special assignments.

Mr. Haley has been associated with Columbia-Southern in an executive sales capacity since 1934, having formerly served as Director of Sales and during the past three years, as assistant to the vice president.

## L.O.F. OFFICERS REELECTED

Directors of Libbey-Owens-Ford Glass Company reelected all officers, headed by John D. Biggers, chairman, and George P. MacNichol, Jr., president.

Other officers include Curtis W. Davis, executive vice president—production; F. Earle Cazayoux, vice president—finance; Stuart S. Wall, vice president and general counsel; Edward M. Everhard, vice president—sales; L. Glenn Bryan, vice president; William H. Hasselbach, vice-president—engineering; Ross S. Carey, secretary; Richard M. Weter, treasurer; Harry B. Ryan, comptroller.

## PATENT AND TRADEMARK PROBLEMS TO BE DISCUSSED

Patent and trademark problems affecting the glass industry, as well as many other industries in world trade, were considered at the Biennial Congress of the International Association for the Protection of Industrial Property in Washington, D. C., May 28 to June 2.

This international organization is concerned with the protection of patents, trademarks, service marks and other industrial property rights through treaty agreements. The association now represents 52 countries and, in effect, is a "United Nations of Trade and Industry."

Nearly 400 American firms, including industrial leaders in many fields, are affiliated with the international association. The American group is known as the International Patent and Trademark Association, and its president is Beverly W. Pattishal, of Chicago. Representing the glass industry in this group are the Corning Glass Works, Libbey-Owens-Ford Glass Company and Owens-Illinois Glass Company.

More than 600 delegates from all parts of the world, including patent attorneys, scholars, inventors, government officials and industrial leaders were expected to attend the Congress.


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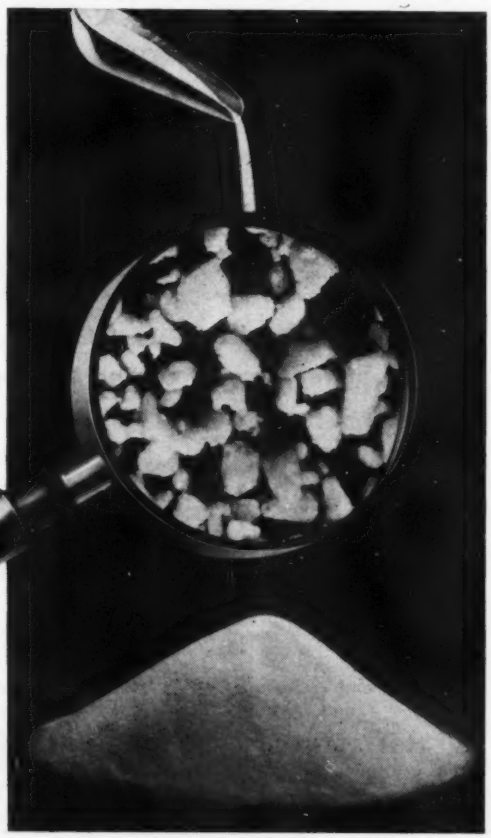

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